AMERICAN

DYESTUFF REPORTER

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Official Publication of the Proceedings of the American Association of Textile Chemists and Colorists

American Dyestuff Reporter was founded in 1917 and the Textile Colorist and Converter (formerly Textile Colorist) was incorporated with it in January, 1949. Published every other Monday by the **HOWES PUBLISHING COMPANY, INC., 44 E. 23rd Street, New York 10, N. Y. C R Howes**, President; **Ernest J Finan**, Executive Vice-President; **Norman A Johnson**, Vice-President & Treasurer; **Myron D Reeser**, Vice-President; **C Essenbreis**, Secretary

Also Publishers of
HOSIERY INDUSTRY WEEKLY
HOSIERY MERCHANDISING

September 29, 1952
VOLUME 41 NUMBER 20

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AMERICAN
DYESTUFF REPORTER

VOLUME 41 September 29, 1952 NUMBER 20

CONTROLLED VAT DYEING*

PART I—THE STABILIZATION OF VAT DYES AT ELEVATED TEMPERATURES

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The trend in vat dyeing today is toward higher temperatures of application, especially in the high-speed continuous processes and package dyeing. Many vat dyes in the leuco state are not stable at these elevated temperatures because they are subject to "decomposition" reactions, one of which is over-reduction. This creates many problems for the dyer in maintaining the uniformity of the true shade. It has been found that the leuco compounds of vat dyes can be prevented from over-reducing by the addition of any one of several compounds, particularly certain nitrogen compounds, to the dyebath. Extensive laboratory and mill runs have demonstrated the reliability and simplicity of the use of these compounds in protecting reduced vat dyebaths at elevated temperatures. The chemistry of this process has been studied and a kinetic mechanism is proposed to explain the protective action of these materials.

INTRODUCTION

VAT dyes, normally insoluble in water, can be dissolved by reduction to the leuco compounds, which are soluble in caustic soda. The reduction must be controlled because many vat dyes are capable of existing in several leuco forms depending upon the degree of reduction. It is undesirable for the reduction to progress too far, because under pratical dyeing conditions, over-reduction is essentially irreversible. If over-reduction occurs, most dyes are changed in shade or destroyed. For this reason, the stability of the leuco to over-reduction is of great importance in vat dyeing, especially when the reduction occurs at high temperatures.

In a pre-war I G publication, formerly restricted in circulation but now available as a P B report of the U S Department of Commerce (*18*), appears a discussion of the undersirable reactions to which the sodium leuco compound of specific vat dyes are subject. These reactions are over-reduction, hydrolysis, molecular rearrangement, crystallization and sensitivity to light, hard water and dyeing assistants. These undesirable reactions have also been under investigation in our laboratories for a number of years. In 1948 Clark (*3*) examined the behavior of the leuco compounds of many vat dyes at 200° F and discussed in particular the practical implications of three of these undesirable reactions (over-reduction, hydrolysis, and molecular rearrangement), when selecting vat dyes for use in continuous dyeing systems at high temperatures. Clark pointed out that the addition of specific types of dextrines and lignin sulfonates strongly inhibit the undesirable effects of high temperature reduction of the leuco compounds of vat dyes.

In 1948 McCleary (*8*), studying the reduction of Vat Blue BLD in our laboratories with the Dyeometer (*6*) found that: (a) in the reduction of Vat Blue BLD at elevated temperatures the leuco form is more stable if minimum quantities of caustic soda (NaOH) and sodium hydrosulfite ($Na_2S_2O_4$) are used; (b) the presence of dextrine in the leuco bath has a marked effect in preventing over-reduction; (c) the type and source of dextrine does not appear to be important; and (d) it is important that the dextrine be added to the bath immediately after the $Na_2S_2O_4$, not before.

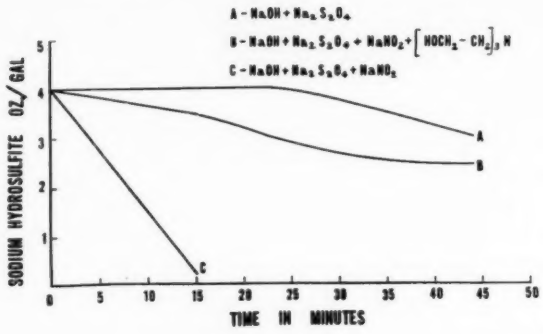
GENERAL DISCUSSION

Work has continued in the study of stabilization of vat dye leucos because it was recognized that the use of dextrines is at best only a partial solution. Due to the reaction of dextrine with caustic soda, large amounts of dextrine must be used in order that an active excess be available to stabilize the vat leuco. Shade control is difficult. The reproducibility and duration of stabilization against over-reduction is low and it is necessary at times for the dyer to throw away large batches of over-reduced dye. Frequently several hundred gallons of expensive booster liquid must be discarded and replaced with fresh material.

During experiments on vat dyeing at elevated temperatures in our laboratory, it was found that the leuco compound of vat dyes could be prevented from over-reducing by the addition of any one of several compounds, particularly certain nitrogen compounds, to the dyebath. Based on these studies, six patent applications were filed with the United States Patent Office on November 30, 1949, and the patents were issued subsequently (*9, 10, 11, 12, 13, 14*). Among the more effective of these patented agents are the inorganic nitrites and the hydroxylamines. For example, a 400-ml dyebath containing 0.35 *g* Calcosol Blue BLD Double Paste, 3 g sodium hydroxide, 3 g sodium hydrosulfite and 1 *g* sodium nitrite was held in the reduced state for 15 minutes at 200° F.

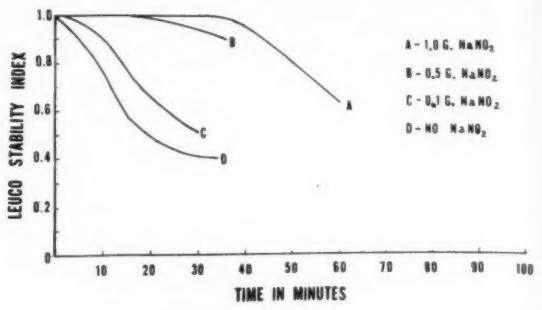
* A series of three papers by members of the Application Research Department, Calco Chemical Division, American Cyanamid Company, Bound Brook, N J.

EFFECT OF TRIETHANOLAMINE ON HYDROSULFITE CONSUMPTION



I—Figure 1

THE EFFECT OF VARYING AMOUNTS OF SODIUM NITRITE ON THE STABILIZATION OF VAT BLUE BLD AT 83°C.



I—Figure 2

A 5 g cotton skein was then entered and dyed for 15 minutes at the boil. The dyed skein was approximately equal in shade and strength to a similar dyeing made in the normal manner at 120° F. In a similar bath containing no nitrite the dye over-reduced in a few minutes. In order to impose an even more severe test, this same dye has been reduced and dyed in the presence of sodium nitrite at temperatures as high as 250° F (under pressure) for short periods of time with no noticeable decomposition or over-reduction of the dye.

Early tests showed that when low concentrations of caustic soda and sodium hydrosulfite were used, such as would be used in jig dyeings, the reaction between sodium hydrosulfite and sodium nitrite was so slow that the hydrosulfite consumption was negligible. The concentration of hydrosulfite was measured by indigo titration. When the concentrations of caustic soda and sodium hydrosulfite were increased to strengths normally used in continuous dyeing, however, a very rapid reaction between nitrite and hydrosulfite occurred. This reaction was so rapid at times that it was impossible to maintain sufficient hydrosulfite in the dyebath to keep the dye reduced. Upon further research it was found that a number of materials, when added to the dyebath, would greatly reduce the rate of reaction between nitrite and hydrosulfite. Among the best of these materials were magnesium salts (*15*), manganese salts (*5*) and triethanolamine (*15*).

In Figure 1, where hydrosulfite concentration is plotted against time, it can be seen that, when a solution containing 4 oz/gal of sodium hydroxide, 4 oz/gal of sodium hydrosulfite and 1 oz/gal nitrite reacts at a rapid rate, all of the hydrosulfite is consumed at the end of about 15 minutes. When no sodium nitrite is present, the mixture shows little loss in hydrosulfite concentration after 25 minutes at 93° C. By adding as little as 0.25 oz/gal of triethanolamine to the solution containing sodium nitrite the loss of hydrosulfite is very greatly reduced. The addition of Vat Blue BLD to the bath appears to have very little effect upon the rate of reaction in the above cases. It seems probable that the action of triethanolamine, manganese salts, and magnesium salts does not influence significantly the stabilization of the dye.

Observations such as these have made possible new and improved methods of applying vat dyes at high temperatures. Many dyers have taken advantage of such stabilization methods to improve both their processes and their products. For example, in many plants the common method for dyeing blue shades on packages has been to apply the dye pigment at 190°-200° F and then lower the temperature from 120 to 140 degrees F before reducing the dye. When proper amounts of sodium nitrite are added to the dyebath, however, it is no longer necessary to lower the temperature before adding the reducing agent, since there is no longer danger of over-reduction. Dyeing at the higher temperature not only reduces the time required but frequently gives better penetration and levelness and eliminates "cross-overs". This was illustrated recently in a mill that had been unable to dye a light blue shade on cotton packages with regular vat dyes and obtain level dyeings. For this reason the mill had found it necessary to use the more expensive soluble vats. It was thought that the unlevelness was due to the low dyeing temperature that had been used to avoid over-reduction. With sodium nitrite added to the bath and the temperature was raised to 180° F and bright level dyeings were obtained with regular vat dyes.

Due to the problem of insufficient stability many hosiery dyers found it necessary to substitute the brominated indigo types for the indanthrone blues in their blue shades. When sodium nitrite is added to the dyebath, however, over-reduction is no longer a problem and full advantage can be taken of the better fastness properties of the indanthrone blues and their more desirable shade. Large scale mill dyeings on hosiery have shown that a good union between cotton and nylon can be obtained with such dyes as Calcoloid Blue BLFD Double Paste if applied at elevated temperatures with sodium nitrite as a stabilizer.

In practical mill runs with indanthrone vat blue dyes in the Williams unit, in which sodium nitrite is used instead of dextrine, it has been possible to decrease the blue dye in the pad formula up to 20% and to show marked savings in the cost of chemicals consumed in the unit bath. In every case over-reduction was completely prevented and, as a result, uniformity of shade from start to end was excellent. The saving of dyestuff has resulted in a material reduction in processing costs. For example, one lot of 40,000 yards of 2.65 mercerized cotton jeans was dyed with 5 oz/gal of dye, the major portion of the dye being Calcoloid Blue BLFD Double Paste. Sodium nitrite was added to the two Williams units and this run, made at 200° F, showed no shading from start to finish or from side to center. Prior to this run it had been found difficult, using dextrine, to prevent shading at 170° F and impossible to run at 200° F. By using the nitrite stabilizer the dye and chemical costs were reduced 11% in this run, making a saving of approximately ¼ cent per yard. The fastness to crocking and to washing was found to be considerably better than in earlier runs with dextrine.

Not all vat dyes over-reduce in the leuco state at elevated temperatures. However, in order to investigate completely the effect of sodium nitrite, a large number of vat dyes have been tested by making dyeings both with and without sodium nitrite. Some of the dyes that were found to be improved by the addition of sodium nitrite are listed in Table I. These dyes were tested by reducing the dye for five minutes at 200° to 212° F and then dyeing for 60 minutes at the same temper-

atures. It should be pointed out that many dyes do not over-reduce as fast after they have been sorbed by the yarn as they do in the dyebath. For this reason, in order to obtain a severe test, it was considered important in making these tests to allow the dye to reduce for several minutes at the elevated temperature before entering the skein. In the case of the dyes which were not improved by sodium nitrite, no evidence was observed indicating that the presence of this material in the dyebath had any deleterious effects on the dyeing.

Since the chemistry of the over-reduction of the indanthrone blues is well known (*1, 2, 4*), Vat Blue BLD (C I 1113) was used in most of this study. In considering the mechanism by which sodium nitrite stabilized the leuco of Vat Blue BLD, there seemed to be several possibilities as: (a) sodium nitrite might reduce the oxidation-reduction potential to a value too low to permit over-reduction and yet high enough to reduce the dye to its "normal" leuco; (b) sodium nitrite might react with the dye producing a stabilized form; and (c) sodium nitrite might act as an inhibitor preventing over-reduction.

The effect of sodium nitrite upon the oxidation-reduction potential was considered first. In 1948 the Intersectional Contest Committee of the Piedmont Section of the AATCC, while studying the high temperature stabilization of vat dyes with dextrines, pointed out that the correlation between their dyeings and the reduction potential of the dye bath aided them in arriving at definite conclusions (*16*). They predicted that the potentiometer would play an important part in future investigations regarding the proper reduction potentials to be maintained when dyeing vat dyes. At about the same time in Germany, Schaeffer (*17*) was studying the use of redox potentials as a means for controlling vat dyebaths. He showed that there is a definite reduction potential for each vat dye and if the reduction potential falls below this value, the dye will be reached only partially or not reduced at all.

Recently Marnon (*7*) has suggested that vat dye baths be controlled by measuring the potential continuously between a bright platinum electrode and a saturated calomel electrode immersed in the dyebath. He acknowledged that by adding sodium nitrite and hydroxylamine to the dyebath, the indanthrone blues could be dyed at elevated temperatures without over-reduction. The use of these agents to control vat dyeing had been disclosed by us to the industry and is covered by patents (*9, 13*). Marnon suggests that the reason over-reduction does not occur is that sodium nitrite has a poising action on the potential of the dyebath reducing it to a low value, 925-950 m v, and that this potential, though high enough to reduce the blue dye, is not high enough to over-reduce it. Results obtained in our laboratories indicate that when sodium nitrite is added to the dyebath there is a rapid change in the potential between the calomel and bright platinum electrodes in the direction corresponding to less reducing power and, with nitrite present at these low potentials, no overreduction occurs. The presence of sodium nitrite or another stabilizer is essential, however, if over-reduction is to be prevented. When a still lower potential was maintained by adding only very small quantities of sodium hydrosulfite to a dyebath containing no sodium nitrite, over-reduction took place in a few minutes.

TABLE I

DYES STABILIZED BY SODIUM NITRITE AT ELEVATED TEMPERATURES

Calcosol Black BB	C I 1102
Calcosol Blue RS	C I 1106
Calcosol Blue GCD	C I 1112
Calcoloid Blue BLD or BLFD	C I 1113
Calcoloid Brown BR	Pr 118
Calcosol Brown RN	C I 1151
Calcoloid Copper Brown	...
Calcosol Flaming Orange 2R	C I 1098
Calcoloid Golden Orange RRTD	C I 1098
Calcoloid Golden Orange 4RD	C I 1098
Calco Vat Red Violet RRK	C I 1161
Calcosol Golden Yellow GK	Pr 291

EXPERIMENTAL

A 400-ml dyebath was prepared containing 0.35 g Calcosol Blue BLD Double Paste, 3 g sodium hydroxide, and 1 g sodium nitrite. This bath was heated to 83° C in the Dyeometer and 3 g sodium hydrosulfite was added. The reduction of the dye was followed spectrophotometrically and the potential between a bright platinum and calomel electrode was recorded continuously. The potential of the bath was found to remain at about 850 m v and the spectrophotometer showed there was no over-reduction of the dye for over 40 minutes at this temperature. Another 400-ml bath, using 0.35 g Calcosol Blue BLD Double Paste and 3 g sodium hydroxide, was also heated to 83° C in the Dyeometer, in which case a very small quantity of sodium hydrosulfite was added. A potential of 825 m v was obtained and spectrophotometric curves showed the dye to be completely reduced within one minute. At the end of 10 minutes the dye was over-reduced although the potential had never gone above 850 m v. A cotton skein dyed in this bath had the dull shade typical of over-reduced Blue BLD. It was concluded, therefore, that the change in reducing power due to nitrite as shown by potential measurements is not alone sufficient to explain the ability of nitrite to prevent over-reduction.

The possibility of a reaction between the nitrite and dye was then investigated. Experiments were conducted in which (a) the amount of Blue BLD was held constant and the amount of sodium nitrite varied, and (b) the amount of nitrite was held constant while the amount of BLD was varied. These experiments showed clearly that the length of time the dye was stable was a function of the concentration of both the dye and the sodium nitrite. When the dye concentration was held constant, the addition of more sodium nitrite increased the time during which the leuco was stable (see Figure 2). In Figures 2 and 3 "Leuco Stability Index" is plotted against time. In these graphs the "Leuco Stability Index" is equal to the "Relative Extinction Coefficient at 735 mμ and is an arbitrary measure of the relative extent of leuco decomposition. A leuco bath which showed no decomposition would give a horizontal line across the top of the graph at a "Leuco Stability Index" of 1.0.

When the same amount of sodium nitrite was added in different experiments, the time of stability of the leuco varied inversely with the dye concentration (see Figure 3). These experiments seem to indicate that a reaction occurs involving the dye and nitrite. They also indicate that sodium nitrite is consumed in stabilizing the dye and must be replaced if further stabilization is desired. These conclusions were supported further by the following experiments.

Solutions containing

(a) 3.0 g NaOH + 3.0 g $Na_2S_2O_4$ + 1.0 g $NaNO_2$ per 400 ml,

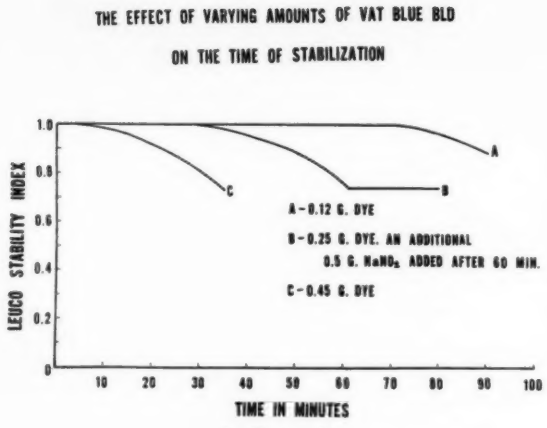
(b) 3.0 g NaOH + 3.0 g $Na_2S_2O_4$ + 0.2 g anthraquinone per 400 ml, and

(c) 3.0 g NaOH + 3.0 g $Na_2S_2O_4$ + 1.0 g $NaNO_2$ + 0.2 g anthraquinone per 400 ml

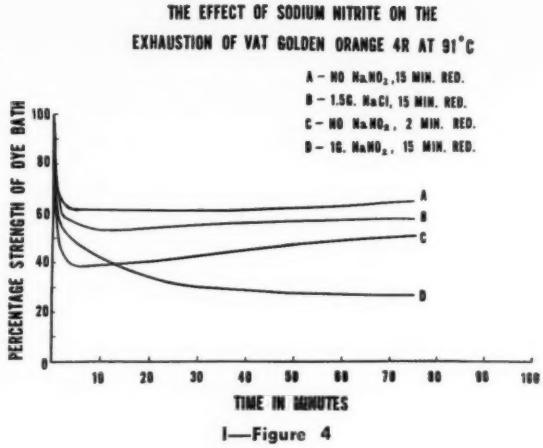
were all heated to the boil. In Solutions A and B, it was possible to obtain a test for hydrosulfite with Vat Yellow G Paper even after boiling for 30 minutes. In Solution C after one minute of boiling no test for hydrosulfite could be obtained and the anthraquinone was precipitated. The first reduction state of Vat Blue BLD, corresponding to the semiquinone form of anthraquinone, is relatively stable due to resonance. This is the "normal" leuco of Blue BLD used in dyeing.

THEORY

The chemical reactions involved in a stabilized vat dyebath are extremely complex. Any theoretical picture must take into account a vast number of experimental facts, many seemingly contradictory. Some assistance may be obtained from the reduction reactions of anthraquinone. When anthraquinone is reduced the semiquinone is never obtained because it is not resonance-stabilized. Not being


THE EFFECT OF VARYING AMOUNTS OF VAT BLUE BLD
ON THE TIME OF STABILIZATION
LEUCO STABILITY INDEX
TIME IN MINUTES
A - 0.12 G. DYE
B - 0.25 G. DYE. AN ADDITIONAL
0.5 G. NaNO2 ADDED AFTER 60 MIN.
C - 0.45 G. DYE

I—Figure 3


THE EFFECT OF SODIUM NITRITE ON THE
EXHAUSTION OF VAT GOLDEN ORANGE 4R AT 91°C
A - NO NaNO2, 15 MIN. RED.
B - 1.5G. NaCl, 15 MIN. RED.
C - NO NaNO2, 2 MIN. RED.
D - 1G. NaNO2, 15 MIN. RED.
PERCENTAGE STRENGTH OF DYE BATH
TIME IN MINUTES

I—Figure 4

resonance-stabilized, it is extremely unstable. As a result it exists only momentarily, proceeding at once to anthrahydroquinone. Alkaline sodium nitrate can act as a mild oxidizing agent. It is believed that sodium nitrite oxidizes anthrahydroquinone back to either semiquinone or anthraquinone and that these compounds are immediately reduced again by hydrosulfite to anthraquinone. This cyclic process continues until either the nitrite or hydrosulfite is consumed. From this, and from the experiments with stabilized dyebaths, the following hypothesis is proposed to explain the stabilization of the leuco of Vat Blue BLD by sodium nitrite.

In the presence of alkaline sodium hydrosulfite the reduction of Vat Blue BLD at elevated temperatures proceeds through the steps in the following equations:

$$(BLD)_{ox} \underset{2}{\overset{1}{\rightleftarrows}} (BLD)_{\text{Leuco I}} \underset{4}{\overset{3}{\rightleftarrows}} (BLD)_{\text{Leuco II}} \xrightarrow{5} (BLD)_{\text{Leuco III}}$$

Leuco I of Vat Blue BLD is the normal leuco form used in dyeing. Reaction 1 proceeds very rapidly in the presence of alkaline hydrosulfite and is easily reversible (Reaction 2). Above 120°F Leuco I is reduced to Leuco II at a moderate rate (Reaction 3). Leuco II, in the presence of alkaline hydrosulfite, is reduced to Leuco III (Reaction 5) at a rate even faster than Leuco I reduces to Leuco II. In an over-reduced solution of Vat Blue BLD, therefore, there is probably very little Leuco II present and the system consists almost entirely of a mixture of Leuco I and Leuco III, at least during the first few minutes. From rate of reaction plots, the change from Leuco I to Leuco III seems to be an autocatalytic reaction and the rate of formation of Leuco III and Leuco II is very slow until an appreciable concentration of Leuco III is produced. It is proposed that sodium nitrite oxidizes Leuco II to Leuco I at a rate which is faster than the reduction of Leuco II to Leuco III. Furthermore, under alkaline conditions Leuco III is not oxidized to Leuco II by sodium nitrite and Leuco I is not oxidized to the oxidized form of Vat Blue BLD or, in any case, only very slowly. Since only a small amount of Leuco II is present at any time and its initial rate of formation is very slow, a small amount of sodium nitrite can reverse this reaction or stabilize the dye for a considerable period of time by preventing the formation of Leuco III.

All of the colors listed in Table I are dyes that are known to be susceptible to over-reduction. However, the mechanism for stabilization of the halogenated pyranthrones (Calcosol Golden Orange RRTD Paste, Calcosol Flaming Orange 2R Double Paste, and Calcoloid Golden Orange 4RD Double Powder) appears to be entirely different from that proposed for the indanthrone blues. It has been found that dyeings made at elevated temperatures with Calcoloid Golden Orange 4R Double Powder using sodium nitrite are much heavier and redder than those made without sodium nitrite. However, Golden Orange 4R was held in the reduced state at 200°F without nitrite for over four hours and no change in the shape of the spectrophotometric curve was observed. This result seems to indicate that any change in the dye molecule is a minor one that does not affect the chromaphore groups, but possibly the auxochrome groups. It can be seen from Figure 4 that if Golden Orange 4RD is reduced for 15 minutes at 196°F in the presence of sodium nitrite and then a 10-g cotton skein is added, the dye is exhausted rapidly, approximately 70% being exhausted at the end of 75 minutes. If, however, a similar dyeing is made without sodium nitrite, less than 40% of the dye is exhausted at the end of 75 minutes. This increased exhaustion is not merely a salting-out effect because, when the sodium nitrite in the dyebath is replaced by 1.5 times as much sodium chloride, only 40% of the dye is exhausted in 75 minutes. (see Figure 4). If the dye is reduced for 15 minutes at 196°F and then sodium nitrite added, the exhaustion is only slightly better than that obtained in the experiment in which no nitrite was added. In Figure 4 it can be seen also that if Golden Orange 4R is reduced for only two minutes without $NaNO_2$ at 196°F before adding the skein, instead of 15 minutes, 60% of the dye is exhausted in the first 5 minutes. Five minutes later, however, the dye starts coming off the skein so that at the end of the 75-minute dyeing period, only 50% of the dye is on the skein.

These experiments seem to indicate that some change is taking place in the dye molecule affecting its exhaustion on the fiber. Vat Golden Orange 4RD is brominated Vat Golden Orange G. The leuco of Vat Golden Orange G is stable at elevated temperatures. Furthermore, it is known that the addition of bromine to Vat Golden Orange G ring structure increases its affinity for cellulose and makes the shade redder. Therefore, it is suggested that the halogenated pyranthrones may lose some of their halogen content when the vat leuco is heated to elevated temperatures causing the dye to lose some of its substantivity to cellulose and become yellower. This is also a form of over-reduction. The addition of sodium nitrite appears to prevent or retard this loss of halogen. Analytical results support this suggested mechanism. Solutions of Calcoloid Golden Orange 4RD Double Powder in the reduced state both with and without sodium nitrite have been heated at 90 to 100°C for 30 minutes, then oxidized, filtered, washed and dried. These samples were analyzed for bromine content and the following results were obtained:

	% Bromine
Golden Orange 4R boiled without $NaNO_2$	16.85
Golden Orange 4R boiled with $NaNO_2$..	21.9
Golden Orange 4R untreated.....	22.75

These results indicate that the addition of sodium nitrite to the Vat Golden Orange 4R dye baths prevents debromination and thereby gives redder and heavier shades.

OTHER STABILIZERS

Although sodium nitrite is one of the most efficient and least expensive stabilizers, a large number of compounds, both organic and inorganic, have been found to be effective *(9, 10, 11, 12, 13, 14)*. Some of the compounds which were found to act as stabilizing agents are shown in Table II. These compounds were tested by reducing Calcosol Blue BLD Double Paste, in the presence of the agent, for five minutes at 200 to 212°F and then dyeing a cotton skein for 60 minutes at the same temperature. In every case, dyeings made in this manner, with the stabilizers shown in Table II, were approximately equal in strength and shade to dyeings carried out at low temperatures in the conventional manner and were greatly superior to dyeings carried out at elevated temperatures without a stabilizer. As a general rule, the compounds that have been found to act as stabilizers are mild oxidizing agents. The inorganic compounds found to work as stabilizers are chlorates, bromates, iodates, nitrites and hydroxylamine. The organic compounds found effective include, among others, nitroparaffins, aromatic nitro and nitroso compounds.

SUMMARY

The trend in vat dyeing today is toward higher temperatures of application, especially in the new high-speed continuous processes and package dyeing. High-temperature dyeing usually improves dye penetration and levelness. It has been shown that the leuco compound of vat dyes can be prevented from overreducing by the addition of sodium nitrite or any one of several other compounds to the dyebath. It has been shown also that the change in reducing power due to the addition of sodium nitrite to the dyebath is not alone sufficient to explain the ability of nitrite to prevent overreduction. A kinetic mechanism has been proposed to explain the protective action of sodium nitrite. The use of sodium nitrite and other stabilizers described in this paper offers a reliable and reproducible method of stabilizing many vat dyes at elevated temperatures and thus gives the dyer many important colors for use in high temperature applications that previously could not be satisfactorily employed.

TABLE II

COMPOUNDS STABILIZING VAT BLUE BLD LEUCO AT ELEVATED TEMPERATURES

Typical Classes of Compounds	*Examples*
Inorganic Nitrites	$NaNO_2$; KNO_2 $LiNO_2$
Inorganic Halogenates	$NaC O_3$; $NaBrO_3$; KIO_3
Inorganic Chlorites	$NaClO_2$
Hydroxylamines	$HONH_2$; $HON(SO_3K)_2.2H_2O$
Nitroparaffins	CH_3NO_2; $C_8H_7NO_2$
Aromatic Nitro Compounds	Nitrobenzene; m-nitrobenzene potassium sulfonate
Nitroso Compounds	n-Nitroso diphenylamine; o-nitroso-m-cresol
Certain Nitrogen Containing Heterocyclic Compounds	3-Phenyl-5-hydroxyisoxazole; 3-(2-ethoxyphenol)-5(4) isoxazone

ACKNOWLEDGMENT

The authors wish to express their appreciation to Dr E E Lineken, who made all of the potential measurements, and to O W Clark and S J Luscian for the information concerning the practical runs. The authors would also like to thank Dr R H Kienle, under whose supervision this work was carried out, for helpful suggestions. The cooperation of other members of our Research and Technical Laboratories is appreciated.

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(15) Mecco, J M, Patent applied for.
(16) Piedmont Section, AATCC, *Am Dyestuff Reptr* 38, 213 (1949).
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PART II—INSTRUMENTAL AND ANALYTICAL MEASUREMENT

G L ROYER

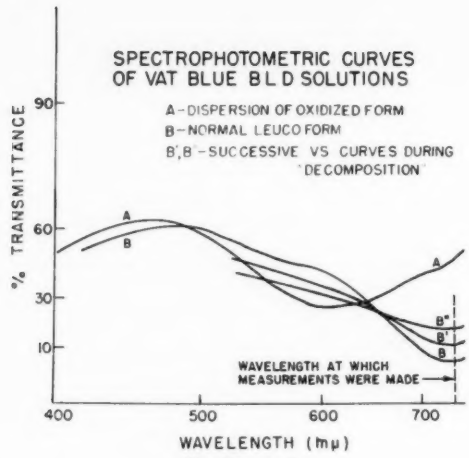
Application Research Department
Calco Chemical Division

INTRODUCTION

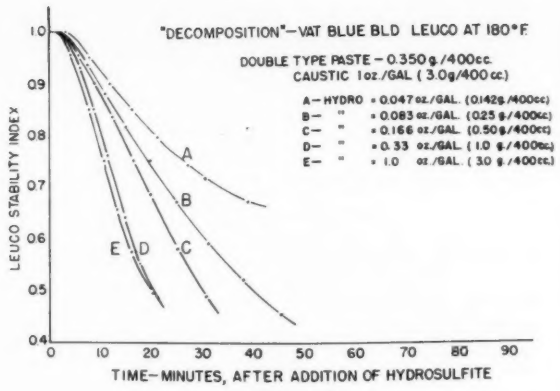
IN our study of vat dyeing over a number of years many instrumental and analytical techniques have been developed and used which have been of value to the dyer. Previous publications from our laboratories have discussed some microscopical, spectrophotometrical and physical chemical methods as they can be applied to the study of package, jig and continuous dyeing of vats. Data on pigment padding, rate of reduction, leuco stability, rate of exhaustion, influence of temperature and addition of leveling agents were given and discussed. In this paper further instruments and control procedures are described and it is hoped that they will be of interest to the dyer to obtain better vat dyeings at a lower cost.

SPECTROPHOTOMETRY

The spectrophotometer is a tool which has found extensive use in our laboratories for studying the application of vat dyes. Fine dispersions of oxidized vat pigments give spectral curves which follow Beers' law so closely that they can be used to determine the concentration of the dispersion. The leuco or reduced form



II—Figure 1


"DECOMPOSITION"-VAT BLUE BLD LEUCO AT 180°F
DOUBLE TYPE PASTE - 0.350 g./400cc.
CAUSTIC 1oz./GAL (3.0g/400cc.)
A-HYDRO = 0.047 oz./GAL. (0.142g./400cc)
B- " = 0.083 oz./GAL. (0.25 g./400cc)
C- " = 0.166 oz./GAL. (0.50g/400cc)
D- " = 0.33 oz./GAL. (1.0 g./400cc)
E- " = 1.0 oz./GAL. (3.0 g./400cc.)
LEUCO STABILITY INDEX
TIME-MINUTES, AFTER ADDITION OF HYDROSULFITE

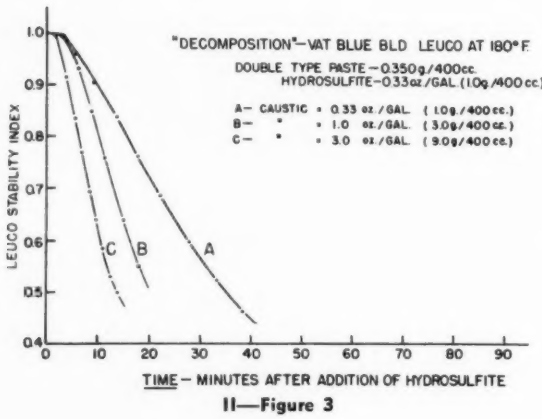
II—Figure 2

of the vat dye usually has a spectral transmission curve quite different in shape from the dispersed oxidized dye. Figure 1 shows the spectral curves for the oxidized, Curve A, and leuco, Curve B, forms of Calcoloid Blue BLFD Double Paste. Spectral data taken at definite time intervals during this reduction can be used to calculate the reduction rates *(1, 2, 3, 4, 5)*.

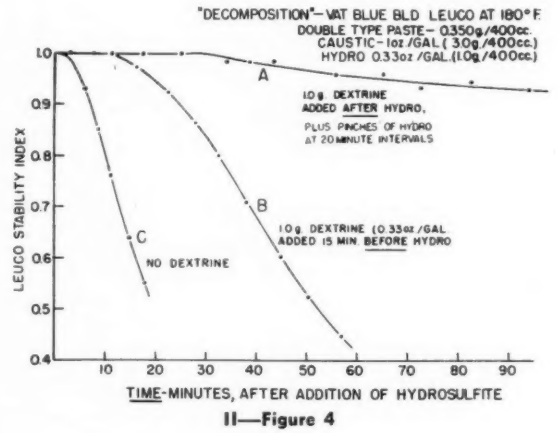
Vat dyes, which are normally insoluble in water, are usually reduced with sodium hydrosulfite in the presence of sodium hydroxide to obtain the soluble leuco form. Since the dye must be in the leuco form for proper exhaustion and fixation, it is important to know if the dye is in the reduced condition and whether there is enough hydrosulfite present to prevent the vat dye from precipitating as the oxidized form. The spectrophotometer is a means of determining the condition of the dyebath, but because of the complications involved, the method is not readily adaptable to dyehouse control. However, for research studies, particularly when the spectrophotometer is used with the Dyeometer (see Figure 6), data can be obtained which are of great value if correlated with practical runs. The minimum concentration of hydrosulfite to keep the dyebath in the proper "leuco potential" range and the minimum concentration of caustic which will maintain the proper pH are readily established by studying the dyes in the Dyeometer-spectrophotometer *(3)*.

The stability of the leuco dye which has been discussed in a previous publication from our laboratories *(6)* must be given serious consideration, particularly if dyeings are being made at high temperatures. At temperatures of 140°F most vat dyes show satisfactory stability for all practical dyeing times. However, as the temperature is raised many vat leuco dyes become quite unstable and at 200°F cannot be used even for short periods because of this instability. This instability has also been studied in the Dyeometer-spectrophotometer. By use of the specially designed thin cell of the Dyeometer *(3)* it is possible to study dyebaths of commercial concentrations. The following experiment illustrates the use of this apparatus in the study of the stability of Vat Blue BLD. The results are typical of those obtained from a number of determinations *(7)*.

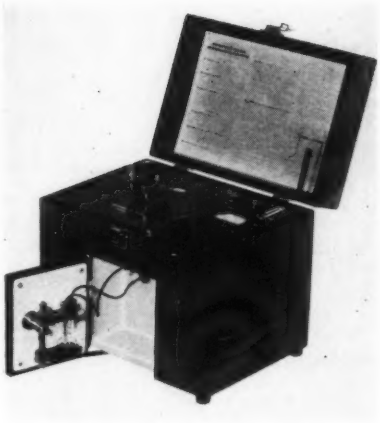
A 400-cc bath containing 0.350 g of Vat Blue BLD Double Paste and 3.0 g (1 oz/gal) of sodium hydroxide was temperature controlled in the Dyeometer at 180°F. Sodium hydrosulfite was added to bring about reduction. The first reduced form of the dye is formed in ten seconds or less at this temperature. The "decomposition", probably a further reduction, starts almost immediately and continues gradually over a period of thirty minutes or more, depending on the conditions of the experiment, leading eventually to precipitation. The spectrophotometric curves of Figure 1 show the color changes involved in the various stages of reduction. Curve A is for the oxidized dispersion of the vat paste in an alkaline solution. The color of the first reduced form is shown by Curve B. Curves B and B" are for successive changes in the "decomposition" of the initial leuco form. This gradual change in color from B to B", etc, was used to measure the rate of over-reduction. These calculations were based on transmission measurements made at a wavelength of 735 mμ on curves traced by a recording spectrophotometer. In Figures 2, 3 and 4, these data are plotted on graphs of "Leuco Stability Index" versus time in minutes


"DECOMPOSITION"-VAT BLUE BLD LEUCO AT 180°F
DOUBLE TYPE PASTE-0.350g./400cc.
HYDROSULFITE-0.33oz./GAL.(10g./400cc.)
A- CAUSTIC = 0.33 oz./GAL. (1.0g./400cc.)
B- " = 1.0 oz./GAL. (3.0g/400cc.)
C- " = 3.0 oz./GAL. (9.0g/400cc.)
LEUCO STABILITY INDEX
TIME-MINUTES AFTER ADDITION OF HYDROSULFITE

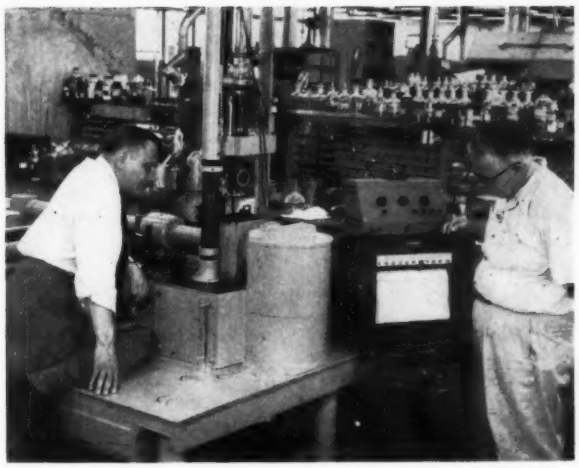
II—Figure 3



II—Figure 4



II—Figure 5



II—Figure 6

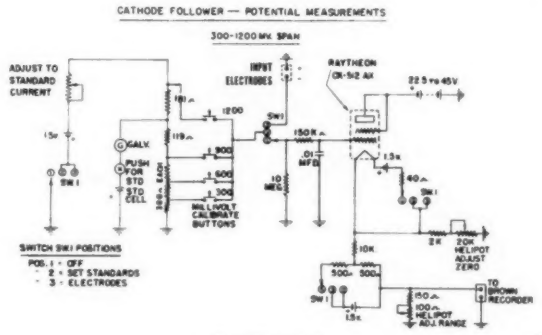
after the addition of hydrosulfite to the bath. The "Leuco Stability Index" is equal to the "Relative Extinction Coefficient" at 735 mμ, and is used as an arbitrary measure of the relative extents of leuco decomposition in the varying experiments. The graph for a leuco bath which showed no decomposition would be a horizontal line across the top of the plot at a "Leuco Stability Index" of 1.0.

Figure 2 illustrates the effect of hydrosulfite concentration on the rate of over-reduction; Figure 3, the effect of sodium hydroxide concentration on the rate of over-reduction; and Figure 4, the effect of adding dextrine on the rate of over-reduction. These are given only to illustrate the use of the Dyeometer-spectrophotometer, since Part I of this series of papers on "Controlled Vat Dyeing" *(8)* has discussed in detail the stabilization of vat dyes at high temperature.

LEUCO POTENTIAL-INSTRUMENTAL MEASUREMENT———The use of potential or voltage measurements between a platinum electrode and a standard calomel electrode is a well known technique used by the physical chemist for studying oxidation-reduction systems, sometimes referred to as redox systems. The analytical chemist also uses this technique to detect the endpoint of titrations in which oxidizing or reducing agents are being analyzed quantitatively. Furman in 1942 *(9)* presented a review of potentiometric titration with reference to 630 papers. A survey made in our library in 1947 revealed an extensive literature on reduction potentials of quinones and vat dyestuffs by such authors as Clar, Clark, Conant, Fieser, Geake and Michaelis. In 1949 A Schaeffer *(10)* discussed the theory of redox potentials and its application in vat dyeing. He presented measurements made potentiometrically and by use of indicator papers on sodium hydrosulfite, formaldehyde sulfoxylate and a number of vat dyes under various conditions of temperature and concentration used in practical vat dye application. Mention was made in the Piedmont Section (AATCC) paper presented at Augusta in October, 1948 *(11)*, of the measuring of reduction potential with a potentiometer but no details were given. A paper by Choquette and Habel *(12)* illustrates the use of reduction potential data as it can be related to the printing of vat dyes of the Blue "BCS" types. More recently Marnon *(13)* in a description of the "Marhen Process" also proposed the use of these potential values, along with suitable agents, for the control of vat dyeing to prevent over-reduction and to obtain a saving in chemicals used for reduction. A commercial potential recorder was recommended by Marnon[1] to obtain the reduction potentials.

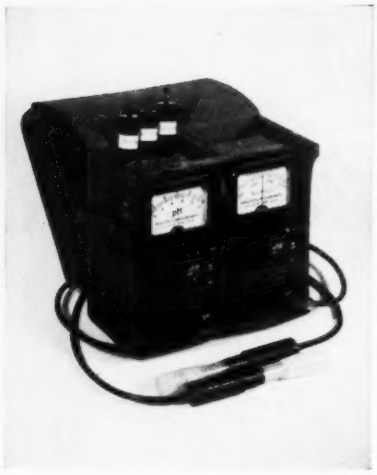
Experiments which have been carried out in our laboratories over the past few years also have indicated that potential values are important in vat dyeing. Other papers in this series on "Controlled Vat Dyeing" discuss the value of what we call "leuco potentials" (LP) of vat dyes and relate these potentials to other important factors. We have defined the "leuco potential" as the potential between a platinum and a saturated calomel electrode at which the leuco vat dye begins to oxidize to the insoluble form. The early measurements made in our laboratory were carried out with a simple potentiometer using platinum and calomel electrodes. A Beckman Model G pH meter[2], reading 0-1300 mv (see Figure 5) can be used. The use of such an instrument is the usual physical chemical technique and similar to that used by Schaeffer *(9)*.

When it became desirable to record the potential data so that it could be more easily related to other measurements being made at the same time, the apparatus shown to the right in Figure 6 was designed (by Calco consultant C W Warren, Warren Electronics, 10 Washington Avenue, Irvington, New Jersey) and connected with a standard Brown Electronik 10 mv strip chart recorder[3]. The circuit for connecting the electrodes and standardizing them for the desired millivolt range is shown in Figure 7. The electrodes used were standard items: Beckman Platinum No 1281-11 and Beckman Calomel



II—Figure 7

(1) Foxboro Dynalog Redox Recorder, Foxboro Company, Foxboro, Mass.
(2) Beckman Instrument Co, South Pasadena, Calif.
(3) Minneapolis Honeywell Reg Co, Brown Inst Div, Philadelphia 44, Pennsylvania.



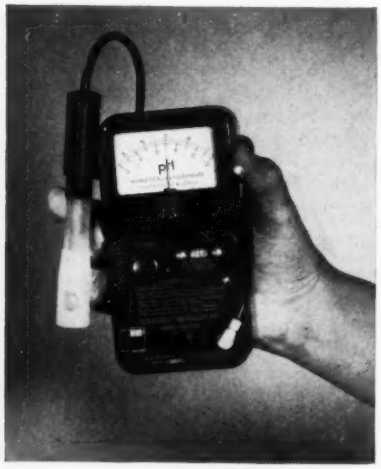
II—Figure 8

II—Figure 10

No 8970. An electronic instrument draws little current from the electrodes during measurement and therefore the electrodes will not become polarized and the readings will be more reproducible and accurate.

While this recording apparatus is quite satisfactory, its relatively high cost led our laboratories to find a meter which was portable and which could be used to indicate the potential in a vat dyebath in the laboratory or in the dyehouse. Such a meter was developed in cooperation with the manufacturer[4] and called a "Leuco Potential Meter". Figure 8 shows this meter in the same case with a pH meter made by the same company. It is also available in a single case without the pH meter. This "Leuco Potential Meter" is easily portable and the electrodes can be inserted into any vat dyebath to determine whether the bath is within the proper "leuco potential" range. The meter is standardized against a self contained standard cell and reads from 700-1,000 millivolts. If one wishes to read values above 1,000, the standardization point can be adjusted to another point on the meter which is lower and the meter reading corrected. For example, the standard value for reading 700-1,000 millivolts is 1,020. If the standard is set to 920 the meter would read from 800 to 1,100 mv and 100 would have to be added to each meter reading in order to obtain the correct "leuco potential". A meter is being designed to read potentials from 0 to 1200 mv in 300 mv ranges. While this small meter is not recording, its portability and reasonable price are attractive features. It can be moved readily from bath to bath for readings or it may be mounted near one bath and the electrodes installed for continuous operation. Its battery operation eliminates permanent electrical wiring and its readily available hearing-aid type batteries provide 1,300 hours of operation.

(4) Analytical Measurements, Inc, 585 Main St, Chatham, N J.



II—Figure 9

The Beckman model N pH meter (see Figure 10) is a portable direct reading instrument which is calibrated in pH units, but it can be adapted by the following procedure to read potentials. (Taken from private communication of G D Butler, Beckman Instruments, Inc, 1114 First Avenue, New York 21, N Y). If the calomel and glass electrodes which are used for pH determinations are replaced with calomel and platinum electrodes, the instrument can be used to read potentials in the range of 0 to 840 millivolts. To standardize the instrument, the temperature control is set at 30°F and the electrode jacks are connected together to short out the input. With the selector switch set at the 0-8 position, the standardization knob is adjusted until the meter reads 0. The short is removed and the electrodes are then connected so that the readings will be negative, i e, the calomel electrode is connected to the glass electrode input terminal and the platinum electrode is connected to the terminal to which the calomel electrode is connected normally for pH readings. The meter is then ready for measurement of potentials. Each pH unit under these conditions equals 60 millivolts, i e, each scale division is 6 millivolts. Higher potentials of 280-1120 millivolts can be read on this meter, if the meter is standardized against a standard cell having a voltage of 1020 millivolts. The cell is connected to the meter input and the meter, set at 30°C, is adjusted to a pH of 12.3 with the standardizing knob. 0 pH is then 280 millivolts and 14 pH is 1120 millivolts, each pH unit being 60 millivolts. Attachment of calomel and platinum electrodes now makes this pH meter a potential meter with a range which can be used to measure the leuco potentials of vat dyes.

LEUCO POTENTIAL-TEST PAPERS ———Schaeffer *(10)*, as mentioned earlier, used dyes as indicators of redox potential changes. In a manner similar to the use of indicators for pH measurement, certain dyes can be used for the approximate measurement of potentials when their color begins to change from the oxidized to the leuco form. Schaeffer presented a series of vat dyes to cover a wide range of potential values. Ten vat dyes were chosen from this list by our laboratory which were in the potential range desired in our study of controlled vat dyeing. Each was made into a test paper by adding 2% of the dye in a reduced form to bleached sulfite pulp. Aeration action of the beater roll oxidized the dye in a short time. These ten dyes, with their oxidized color, their reduced or leuco color, their "leuco potentials" and the potentials as determined by Schaeffer are given in Table I.

TABLE I

Dye	Oxidized Color	Reduced Color	Leuco Potential*	rH Complete Reduction	rH First Color Change
Calcosol Golden Yellow GK Dbl Pst	Golden Yellow	Red-brown	...	3.8	7.0
Calcosol Yellow G Dbl Pst	Yellow	Blue	770	4.0	7.5
Indanthrene Yellow GF (General)	Yellow	Brownish-black	...	2.4	4.5
Calcosol Golden Orange G 100%	Golden Orange	Maroon	945	0.8	3.6
Calcosol Khaki G Dbl Pst	Khaki	Red-brown	980	0.8	2.6
Calcosol Brown R 100% Pdr	Brown	Red-brown	1000	1.8	4.8
Calcosol Blue RS Dbl Pst	Blue	Greenish-blue	...	1.5	..
Calcoloid Dark Blue BOD Dbl Pdr	Dark Blue	Dark reddish-violet	...	1.6	..
Calcosol Jade Green N Supra Dbl Pst	Green	Deep blue	960	1.8	4.3
Calcoloid Black BBD Dbl Pdr		Violet	940		

* Values determined at 205°F, 0.5 oz/gal of caustic and 0.2-0.4 oz/gal of dye.

As in the use of pH indicators these papers can be used to indicate the approximate "leuco potentials" of vat solutions, but with much less precision than can be obtained with electronic measuring instruments. A comparison of the r_H potentials determined by Schaeffer and our "leuco potential" values shows some discrepancies. These potentials should not check, since they were determined under different conditions and are not defined or calculated the same. Our "leuco potential" value would be between Schaeffer's two values and should be closer to the r_H for complete reduction. Even with this variation, the papers can serve as indicators of high or low dyebath potentials and be of some use. For example, we find Yellow G reduces easily, while Golden Orange G reduces more difficultly. Other dyes are even more difficult to reduce and can be chosen if such an indicator is desired. Vat Yellow G test paper, because of its low reduction potential, many times has given false results for excess hydrosulfite. It can be reduced by the leuco of vat dyes having higher leuco potentials in baths that contain no excess of hydrosulfite. This should be kept in mind in using vat dye papers as indicators. In addition to choosing the paper with the proper "leuco potential", attention should be given to choosing a dye with a marked color change from oxidized to reduced form so that the change can be easily recognized in colored dyebaths.

pH MEASUREMENT ——— Alkaline conditions, usually obtained by sodium hydroxide, are needed to maintain the proper pH during reduction with hydrosulfite and to form the soluble sodium salt of the leuco or reduced dye. pH indicators or indicator papers can be quite useful when adjusting the alkalinity of the leuco dyebaths, but if one desires more precise control, a pH meter is more reliable. A number of electronic glass electrode pH meters are available on the market and recently several have been designed which are direct reading, battery-operated and readily portable. Figure 9 shows the Analytical pH meter (Analytical Measurements Co*) and Figure 10 the Beckman Model N pH meter (Beckman Instrument Co**). In Figure 8 the "Analytical pocket-size pH meter" is shown in a combined case with the "Leuco Potential Meter" which we have developed in cooperation with the manufacturer.

The regular glass electrode which is satisfactory for the measurement of pH in the range of 0 to 10 at low temperatures is not satisfactory for measurements in high alkalinities at high temperatures. Electrodes made from special glass, e g, Beckman No 8990-90 or similar ones made by other manufacturers, are available for use under these conditions and should be used in pH meters for measurement of leuco vat dyebaths. The proper use of pH measurements will aid in maintaining the stability of vat leuco baths at high temperatures as shown in Figure 3 as well as in avoiding the use of an excess of sodium hydroxide. There are, however, dyes which require high concentrations of caustic to prevent certain types of over-reduction and the user needs to know what type of dye he is concerned with in choosing the proper pH. The pH must be high enough to keep the leuco vat dye in solution for proper dye exhaustion and to prevent the formation of the insoluble acid leuco which does not, under normal dyeing conditions, penetrate or diffuse into the textile fibers for proper dyeing. Titration with acid would be used to determine the total quantity of alkali present.

* See footnote 4.
** See footnote 2.

HYDROSULFITE DETERMINATION

As discussed in Part III of this series, which immediately follows this paper, the potential measurement and the known "leuco potential" of the dye used enables the dyer to know whether the vat dye in the bath is in the soluble leuco form but it does not tell how much reserve hydrosulfite is in the bath *(14)*. It has been inferred by Cayce *(15)* that reduction potential can be used to determine the amount of excess hydrosulfite. In electrical measurements the "pressure" of the system is the potential and is measured in volts. The quantity of electricity that flows in a unit time is measured in amperes. In acid-base reactions, the potential of the glass electrode is related to the pH but the reserve or available acid or base must be determined by titration particularly when other chemicals are present. A similar relationship is also true in determining the quantity of a reducing agent.

We have used the term "leuco potential" and defined it as the potential between a platinum and a calomel electrode at which the leuco vat dye begins to oxidize to the insoluble form. It is a specific value for each dye for each set of bath conditions. None of the potential readings measure the concentration or reserve of hydrosulfite. When this information is desired the excess is best determined by titration or with the polarograph. It should be emphasized that "leuco potential" is related to the reduced form of the dye and not to the potential of the hydrosulfite. It is true that once the dye has been reduced at its "leuco potential" with a reducing agent, such as hydrosulfite, any large excess quantity of hydrosulfite is unnecessary. "Leuco potential" values can serve as a guide to prevent the use of an excess of reducing agent but cannot be relied upon to determine the amount present. The addition of excess hydrosulfite beyond the amount necessary to reduce the dye will result in large potential readings but they do not necessarily have any significance in relation to the quantity of excess hydrosulfite.

An article by Furness *(16)* discusses the analysis of hydrosulfite by both chemical titration and the polarograph. A number of references to the literature are given and he describes three chemical methods: a) reduction of indigo carmine; b) reduction of ammoniacal silver solution; and c) formation of formaldehyde-sulfoxylate and titration of the latter with iodine. A more detailed report on the methods used in our laboratory follows. In most cases it is not necessary to have an exact titration of the hydrosulfite. A rapid method with adequate precision is most desired.

INDIGO TITRATION ——— In the

Du Pont Soda Ash Development Process for the application of vat dyes *(17)* the excess alkali is determined by titration with hydrochloric acid and the excess hydrosulfite is titrated with a standard indigo solution. In their procedure a standard indigo solution is diluted with water in a flask and is titrated rapidly with a portion of the booster bath.

In our laboratories we have also used an indigo method for the determination of hydrosulfite. Our method involves the titration of a measured volume of a standard indigo solution by the hydrosulfite solution which is being measured. The endpoint is determined by the disappearance of the blue color of the oxidized indigo and the appearance of the yellow reduced form.

A solution of disulfonated indigo (made up to contain 6 g/l) was standardized against a solution prepared to contain 1 oz/gal of commercial sodium hydrosulfite and 1 oz/gal of sodium hydroxide. It was found necessary to carry this titration to completion very rapidly in order to prevent the errors which otherwise would be introduced by the reoxidation of the leuco indigo by air. This precaution would not be needed if an inert atmosphere were maintained in the titration flask. The following experimental values were obtained. In each case 10 ml of indigo solution was used.

Test	*Volume Hydro Solution Used (ml)*
1	7.0
2	7.0
3	7.3
4	7.5
5	7.5
6	8.0
7	7.1
Average	7.3

Using this value, i e, each 7.3 ml of reducing solution required to titrate 10 ml of the indigo corresponds to 1 oz/gal of hydrosulfite, titrations were run on known dyebaths. Analyses of four baths, each containing 1 oz/gal of hydrosulfite, 1 oz/gal of caustic and 1 oz/gal of sodium nitrite gave values of 1.0 oz/gal hydrosulfite in each case. Four other similar baths containing in addition 0.1 oz/gal of Vat Blue BLD also analyzed 1.0 oz/gal of hydrosulfite each.

It can be seen that neither the dye nor the $NaNO_2$ interfered with the titration. It seems probable that the great speed and the temperature at which the tests containing the nitrite and dye were made, prevented any loss of hydrosulfite, such as might have been expected when the dye was present. This method is the simplest and most rapid of the approximate titration methods tested. It should be noted that the values are not quantitatively exact in regard to real hydrosulfite. They are relative to the strength of the commercial sample which was used.

IODIMETRIC TITRATION——We have investigated the iodimetric method for the determination of sodium hydrosulfite. This method is dependent upon the measurement of the volume of standard iodine solution required to oxidize the hydrosulfite. It is reliable when no interfering substances are present but we have not found it applicable for titrating dyebaths which contain sodium nitrite and other chemical agents.

The iodimetric method has been found useful for analyzing sodium hydrosulfite powder to determine its "real" content. The sample is treated with neutralized formaldehyde to yield the formaldehyde bisulfite and formaldehyde-sulfoxylate compounds. Only the formaldehyde-sulfoxylate reacts with iodine. Other reducing compounds must be assumed to be absent. Any sodium thiosulfate would consume iodine. The procedure used in our laboratories for the actual analysis follows: Measure in a graduate cylinder 35 ml of 37% formaldehyde solution and 50 ml of distilled water, pour them into a beaker and mix thoroughly. Add just enough N/10 NaOH to turn litmus paper blue. Now transfer 50 ml of this mixture into a standardized 500 ml volumetric flask, and place a dry funnel in the neck of this flask. The other 35 ml of the diluted formaldehyde solution is reserved for later use. Accurately weigh approximately 8.00 grams of the well mixed sodium hydrosulfite in a stoppered weighing bottle. Set the solution in the flask in motion by gently twirling the flask and pour the entire sample into it through the dry funnel. Keep the contents in motion to prevent caking and decomposition. There is sufficient formaldehyde in the solution to react with all of the hydrosulfite converting it to the sulfoxylate. *Caution:* if the material is allowed to lie in the bottom of the flask, there will be a local deficiency of formaldehyde at this point and the heat of reaction will be sufficient to decompose the hydrosulfite which has not been converted to sulfoxylate. Wash out the weighing bottle with the 10 ml of formaldehyde solution which has been reserved and rinse down the sides of the funnel and the neck of the flask. Make up to the mark with distilled water and mix well.

Pipette a 10-ml aliquot into a 300-ml Erlenmeyer flask, dilute to 100 ml with distilled water, add 5 ml of 20% acetic acid and titrate with N/10 iodine using starch as an indicator. The percent sodium hydrosulfite can be calculated by the following formula:

$$\text{Iodine Value as \% } Na_2S_2O_4 = \frac{\text{ml N/10 Iodine x 21.77}}{\text{g Sample}}$$

FERRICYANIDE TITRATION——Tests have also been made using ferricyanide titration for the determination of hydrosulfite. In the ferricyanide method a measured volume of the bath having an unknown amount of hydrosulfite is titrated with a standardized solution of potassium ferricyanide. The endpoint is determined by spot tests on Vat Yellow G test paper. The ferricyanide solution, made up to contain 32.9 g/l of potassium ferricyanide, is standardized against a solution made up to contain 1 oz/gal of commercial sodium hydrosulfite and 1 oz/gal of NaOH. In this method it is important that a minimum of agitation be employed during the titration in order to prevent oxidation of the hydrosulfite by the air. A gentle swirling motion is recommended for stirring. Also, the titration should be completed as rapidly as possible. When these precautions were used it was found that 6 ml of the ferricyanide solution were required to titrate the hydrosulfite in 10 ml of the hydrosulfite and caustic mix. Four separate titrations checked within the limits of the volumetric measurements. Based on this value, i e, each 6 ml of the ferricyanide solution required to titrate 10 ml of reducing solution corresponds to 1 oz/gal of the hydrosulfite, several titrations were made (see Table II).

It can be seen, from experiments 1-4, that the presence of the $NaNO_2$ did not interfere with the determination of the hydrosulfite. The lower values from the last three solutions probably show that there is a reaction of some of the hydrosulfite with the nitrite in the presence of the dye.

VAT-OMETER METHOD ——— We have also studied the Vat-Ometer for determining sodium hydrosulfite. The Vat-Ometer provides a method for measuring hydrosulfite concentrations and is simple to use *(18, 19, 20, 21)*. Briefly, this instrument measures the amount of oxygen absorbed from the air by the hydrosulfite present in a measured volume of dyebath. By calibrating the instrument these volumes become translatable at once into oz/gal of hydrosulfite.

A model of a Vat-Ometer was built and tested. In order to check the practicability of the instrument, several determinations were made. Four separate reducing solutions were prepared for these tests as follows:

a) For calibration of the Vat-Ometer 1 oz/gal NaOH and 1 oz/gal $Na_2S_2O_4$
b) Like (a) plus 1 oz/gal of $NaNO_2$
c) Like (a) plus 0.05 oz/gal Vat Golden Orange 4RD double powder

TABLE II

No	Solution Titrated*	oz/gal of Hydro Found
1	Contained approximately 1 oz/gal of $NaNO_2$	0.96
2	Contained approximately 1 oz/gal of $NaNO_2$	1.0
3	Contained approximately 1 oz/gal of $NaNO_2$	1.0
4	Contained approximately 1 oz/gal of $NaNO_2$	1.0
5	Cont approx 1 oz/gal $NaNO_2$ and 0.1 oz/gal Vat Blue BLD paste	0.7
6	Cont approx 1 oz/gal $NaNO_2$ and 0.1 oz/gal Vat Blue BLD paste	0.7
7	Cont approx 1 oz/gal $NaNO_2$ and 0.1 oz/gal Vat Blue BLD paste	0.9

* Each contained 1 oz/gal of hydrosulfite and 1 oz/gal of caustic.

d) Like (a) plus 1 oz/gal of $NaNO_2$ plus 0.05 oz/gal of Vat Golden Orange 4RD double powder

A 20% solution of Igepon T gel was used as the foaming agent. In each case 10 ml of the hydrosulfite solution was used for the test.

CALIBRATION (SOLUTION "a" USED)

Test No	Volume Air Absorbed (ml)
1	7.2
2	8.2
3	5.2
	Avg 6.8

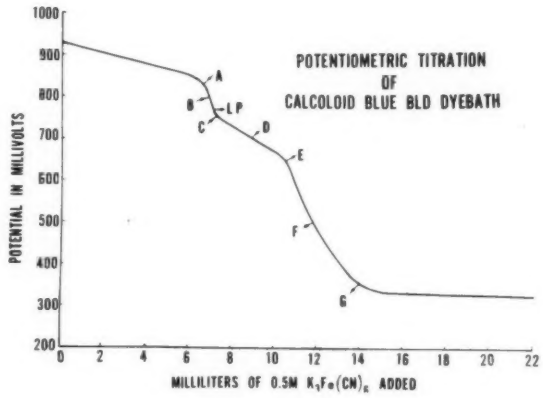
Using this value as a calibration, i e, each 6.8 ml of absorbed air corersponds to 1 oz/gal of commercial hydrosulfite, the following results were obtained for the amount of hydrosulfite present in the other three solutions:

Test No	Solution (b) oz/gal	Solution (c) oz/gal	Solution (d) oz/gal
1	0.7	1.1	0.8
2	1.2	0.8	0.6
3	1.2	1.3	0.8
Avg	1.0	1.1	0.7

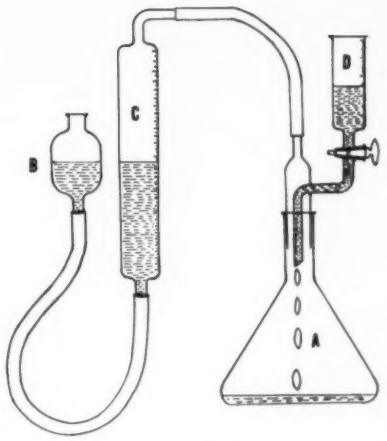
It can be seen from the tests of solution (b) that the presence of $NaNO_2$ did not seem to interfere in the Vat-Ometer method. The lower value obtained for the amount of hydrosulfite in solution (d) again seems to indicate that in this case there has been some reaction between the hydrosulfite and the nitrite when dye is present.

POLAROGRAPHIC DETERMINATION ——— The polarographic method for determining hydrosulfite was first proposed by Brearley and Stackie *(22)*. Furness *(16)* has extended this work and states that "the precision attainable in the polarographic determination of hydrosulfite is seldom as good as in the volumetric processes, but when a probable relative error of about 1% can be tolerated in quantitative work the polarographic method is direct, and often more rapid and sensitive than other methods."

POTENTIOMETRIC TITRATION ———As mentioned earlier in this paper, potential measurements are used by the analytical chemist to detect endpoints of titrations. This technique can be used in the determination of hydrosulfite with an oxidizing agent, such as ferricyanide, iodine, sulfonated indigo or any modification referred to in the discussion of the chemical methods. It must be remembered that these oxidizing agents will under certain conditions titrate other reducing agents other than hydrosulfite if they are present. Therefore, an understanding of the system being studied must be known before the entire quantity of oxidizing agent can be stated to represent the quantity of hydrosulfite in any dyebath. Figure 11 shows the titration curve of a vat dyebath containing Vat Blue BLD, caustic and an excess of hydrosulfite. The milliliters of 0.5 M ferricyanide solution are plotted versus the millivolt values. The change of the curve at A is the point



II—Figure 11



II—Figure 12

where the oxidation of the hydrosulfite is almost complete. The point B between A and C is the endpoint taken for the determination of the hydrosulfite. From points B to F the vat dye is oxidizing and precipitating. The endpoint F between E and G represents the completion of this reaction. The milliliters of ferricyanide from B to F is the amount necessary to oxidize the vat dye and can be used to calculate the amount of vat dye in the dyebath. The "leuco potential", as we have defined it, is near C or slightly higher. This example illustrates the usefulness of potentiometric titrations for analytical purposes and also for a better understanding of the reactions which take place in a vat dyebath.

SODIUM NITRITE DETERMINATION

The decomposition of HNO_2 by sulfamic acid was employed in determining the amount of $NaNO_2$ present in the dyebath, the volume of evolved nitrogen gas being a measure of the amount of $NaNO_2$ originally present. Recently, Brasted *(23)* discussed the reaction of sodium nitrite and sulfamic acid, reviewed the literature and presented an indirect gravimetric method for determining nitrites. In our method 10 ml of the reducing solution to be tested for sodium nitrite was placed in flask A (see Figure 12) and the ground glass stopper tightly seated. The leveling bulb "B" was brought alongside the measuring burette "C" in position such that the levels of the water were the same in both the bulb and the burette, thus bringing the gas inside both the burette and the flask to atmospheric pressure. The reading of the burette at this time was recorded. Fifteen ml of an ammonium sulfamate-acetic acid mix were then run from the dropping tube D into the flask. The flask was shaken gently until no more gas was evolved, as shown

by a constant reading of the water level in the burette. This required about two minutes. The bulb was again brought alongside the burette to a position such that the water levels were the same, thus bringing the gas pressure back to that of the atmosphere, and the burette was again read. The difference between the first and second burette readings minus the volume of solution added to the flask was the uncorrected volume of nitrogen gas evolved. Since the amount of nitrogen gas which was liberated depended only on the amount of $NaNO_2$ which was present, the measurement of this volume provided a convenient measure of the nitrite. A blank run indicated that no difficulty would be encountered from the decomposition of the hydrosulfite.

When 15 ml of a mix containing 25% of ammonium sulfamate by weight and 12.5% of acetic acid by weight were added to a 10-ml sample of a solution containing 1 oz/gal of hydrosulfite and 1 oz/gal of $NaNO_2$, 22.8 ml, uncorrected, of nitrogen gas were evolved. Using this value as a calibration, i e, each 22.8 ml uncorrected volume of nitrogen evolved from a 10-ml sample corresponds to a $NaNO_2$ content of 1 oz/gal, the following measurements were made on the solutions as listed:

Test No	Solution Tested	oz/gal $NaNO_2$ Found
1	1 oz/gal of hydro and of $NaNO_2$....	0.95
2	1 oz/gal of hydro and of $NaNO_2$....	1.05
3	1 oz/gal of hydro and of $NaNO_2$ plus 0.1 oz/gal Vat Blue BLD paste...	1.06

From these values it appears that this simple method for determining $NaNO_2$ will give reliable results.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr R H Kienle, director of the Application Research Department, for his support of this work. The use of experimental data from the investigations of Drs H R McCleary, F Fordemwalt, E E Lineken and S Grand is acknowledged. Advice from J Mecco, C L Zimmerman, F C Dexter and J C Leininger in the preparation of this manuscript is appreciated. The "leuco potential" test papers were prepared by M C Hutchins after the suggestion of Dr W A Raimond. Encouragement to continue our studies has continually been given by our technical service men in this field, S J Luscian and O W Clark. The drawings for the figures were made by Mrs Louise Pesyk. The photographs were furnished by the manufacturer of the equipment, except for Figure 6 which was taken by R R Krammes of our laboratories.

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PART III—LEUCO POTENTIALS

E E LINEKEN, S GRAND and F FORDEMWALT

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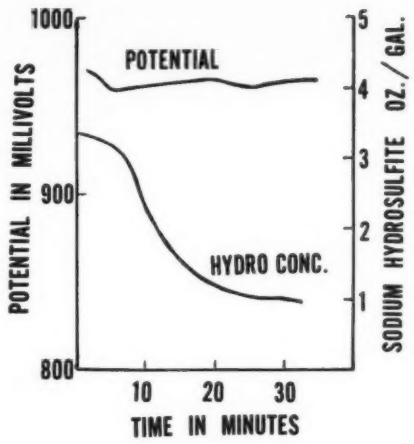
A VAT DYEBATH is a solution containing the dye in its reduced (leuco) state and an excess of sodium hydroxide (caustic) and sodium hydrosulfite (hydro). In the course of dyeing, some hydro and caustic are consumed by air oxidation. When a stabilizing agent, such as sodium nitrite, is present under certain conditions, the consumption of hydro and caustic may become excessive. If the caustic concentration becomes too low, the acid leuco of the dye, which is very insoluble, will precipitate. If the hydro concentration becomes too low, the leuco begins to oxidize with the resulting gradual precipitation of the vat dye. Either of these consequences is serious as far as the dyeing is concerned and it is, therefore, common practice to use large excesses of caustic and hydro in order to assure sufficient amounts of each.

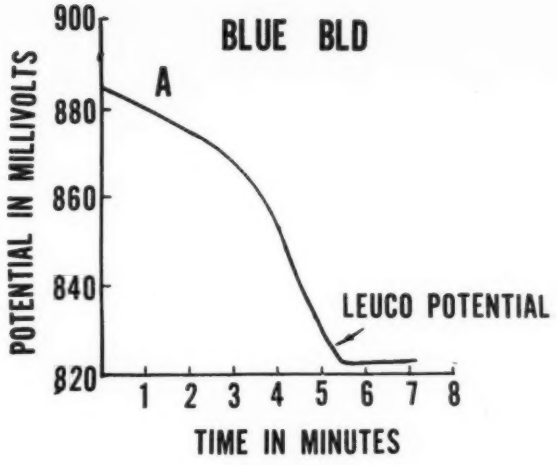
Worthwhile savings would result if these excesses of caustic and hydro could be avoided. While it is possible to determine these substances by rapid chemical analyses, it is both more feasible and more satisfactory to use instrumental methods to indicate when an addition of one or the other substance should be made to the dyebath. These chemical and instrumental methods are described in Part II of this series on "Controlled Vat Dyeing" *(1)*, which immediately precedes this paper.

In the usual case, sufficient caustic is present when the pH of the bath has the correct value for the dye or dyes being used. If the pH becomes too low, an addition of caustic is required. Unless the solution is completely unbuffered, a pH measurement tells little as to the total concentration of caustic present. In other words, pH indicates that there is or is not enough caustic present to prevent the formation of the insoluble acid leuco but it does not tell, except in the unusual case, how much more than the necessary amount has been added. pH measurements can supply instantaneous, simple and exact instrumental warnings when more caustic is needed, which is the information required by the dyer if he wishes to avoid waste of caustic.

The oxidizing or reducing power of a



III—Figure 1



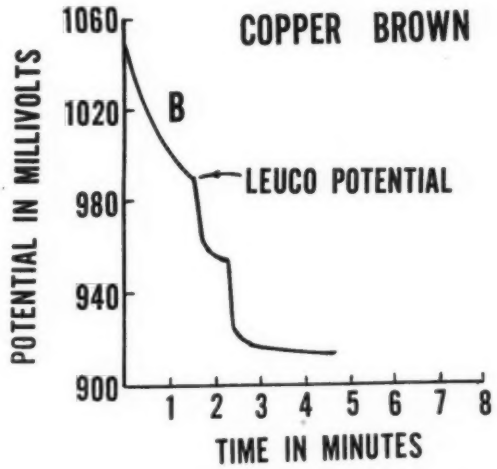
III—Figure 2

solution can be expressed as a potential which is called by one of several names; oxidation, reduction, oxidation-reduction or redox potential. This potential is expressed in volts or millivolts. (The literature of chemical thermodynamics should be consulted for a full discussion of these potentials.) The reducing ability of a solution containing hydrosulfite, sulfite and hydroxide ions, such as is present in a vat dyebath, could be expressed as a potential, but the potential involved is one of those which, as shown by McMillan, Jr, Roberts and Coryell *(2)*, is not satisfactorily measurable. Thus it is not possible to consider that the potential of a platinum electrode immersed in such a solution measures its reducing potential exactly. In addition, a very long time is required before the measured potential approaches a nearly constant value. Even if it were an exact measurement, it would still have to be borne in mind that variations in this potential, according to the reaction usually written for the oxidation of hydrosulfite ion, would depend as much upon the fourth power of the hydroxyl ion concentration and the second power of the sulfite ion concentration as it does upon the first power of the hydrosulfite ion concentration. Potential changes of the bath would thus depend more on changes in the concentrations of other ions than upon changes in hydro concentration. For the above reasons, potential readings cannot be used to indicate hydrosulfite concentrations. This was clearly borne out by measurements made during a Williams Unit run when constant potentials between platinum and saturated calomel electrodes were obtained while the hydro concentration varied between one and three ounces per gallon, as shown in Figure 1. In other cases the potential values have shown no fluctuation regardless of the hydro concentration unless this dropped below 0.25 ounce per gallon.

The oxidation potentials of many substances similar to vat dyes, but made soluble by substituted groups, such as sulfonic acid groups, have been extensively studied by many investigators mentioned in the second paper in this series *(1)*. The electrode equations for the case where an insoluble vat dye is involved have been thoroughly developed by Geake *(3)*, who, in a series of papers, has reported potentials as they relate to many dyes.

DISCUSSION OF LEUCO POTENTIAL

When the hydrosulfite has been consumed, or when it has been almost consumed for the case of dyes which oxidize at high potentials, any further oxidation causes the potential to decrease and the dye begins to oxidize. The potential above which a vat dye is completely reduced or below which the leuco begins to oxidize and precipitate we have called the "leuco potential" (LP). Its value for a given dye depends upon the temperature and the concentrations of the dye and hydroxyl ions in the bath. When the potential drops to the LP value, the hydrosulfite has been exhausted and the reduced-oxidized dye system is beginning to control the potential. The LP is always higher than the midpoint reduction potential of the dye under the same conditions of dyebath composition, temperature, concentration and pH, since at the midpoint potential half of the dye has already been oxidized and precipitated. "Leuco potentials" were found to vary considerably from dye to dye. They are of value to the dyer because when the potential of a dyebath begins to drop, he knows that hydro must be added before the LP is reached, otherwise the leuco will begin to be oxidized. Knowledge of the LP for a dyebath per-



III—Figure 3

TABLE I

Dye	Concentrations oz/gal		Leuco Potentials Millivolts	
	Dye	Caustic	140° F	205° F
Calcoloid Black BBD Double Paste	0.2	0.5	930	940
Calcoloid Direct Black JD Double Powder	.2	.5	900	930
Calcoloid Gray RD Paste	.4	.5	920	960
Calcosol Gray 2G Double Paste	.2	.5	910	1015
Calcosol Dark Blue BO Paste	.4	.5	900	890
Calcosol Blue 2BDG Conc Paste	.2	.5	765	750
Calcosol Blue R Double Paste	.2	.5	955	1035
Calcosol Navy Blue Paste	.4	.5	920	980
Calcoloid Blue BLN Double Paste	0.2[1]	2	...	855
Calcoloid Blue BLN Double Paste	0.8[2]	2	...	870
Calcoloid Blue B L N Double Paste	0.2[3]	1	830	...
Calcoloid Blue BLN Double Paste	2.0[3]	2	870	...
Calcosol Brown RR Single Paste	.4	.5	755	790
Calcosol Brown RR Single Paste	.4[2]	.5	...	780
Calcosol Khaki G Double Paste	.2	.5	1000	980
Calcosol Khaki G Double Paste	.2	1.5	...	975
Calcosol Brown R Double Paste	.2	.5	995	1000
Calcosol Brown BR Paste	.4	.5	970	960
Calcosol Copper Brown Paste	.4	.5	1000	990
Calcosol Jade Green N Supra Double Paste	.2	.5	875	960
Calcosol Jade Green N Supra Double Paste	.2[3]	.5	...	860
Calcosol Jade Green N Supra Double Paste	.2	2	890	955
Calcosol Jade Green N Supra Double Paste	2	2	945	990
Calcosol Olive Green BP Paste	.4	.5	850	950
Calcoloid Olive R Double Paste	.2	.5	960	950
Calcosol Olive T Paste	0.4	0.5	960	1000
Calcoloid Golden Orange RRTD Paste	0.4	0.5	920	995
Calcosol Flaming Orange 2R Double Paste	0.2	0.5	940	910
Calcoloid Golden Orange GD Double Paste	0.2	0.5	950	945
Calcosol Pink FFD Paste	0.2	0.5	720[4]	790
Calcosol Pink FFD Paste	2	1	825[4]	915
Calcosol Red BN Double Paste	.2	.5	880	985
Calcosol Red 2B Single Paste	.4	.5	965	954
Calcosol Violet BN Extra Paste	.2	.5	775	750
Calcosol Violet 4RP Extra Paste	.2	.5	945	980
Calcoloid Violet 6RD Double Powder	.2	.5	785	925
Calcoloid Yellow GCD Paste	.2	.5	930	1000
Calcoloid Yellow GCD Double Powder	.2	.5	900	980
Calcosol Yellow G Double Paste	.2	.5	770	775
Calcosol Fast Yellow Paste	.4	.5	920	930

(1) Stabilized by addition of 2 oz/gal of sodium nitrite and 0.03 oz/gal of magnesium sulfate.
(2) Stabilized by addition of 2 oz/gal of sodium nitrite.
(3) 0.5 oz/ gal of sodium nitrite added.
(4) Accuracy poor because of local precipitation of the oxidized form since it is not re-reduced at 140° F. Also, at the higher concentrations the leuco form is not completely dissolved at 140° F.

mits a dyer to avoid large excesses of hydro and thus to lower his dyeing costs. In order to make use of LP values, it is also necessary to know that the caustic present is sufficient, because a lowering of pH may change the LP for a dye.

LP values might be determined by a procedure such as has been used by Fieser *(4)* in locating exact critical oxidation potentials. It is not necessary to know LP values exactly, however. A rapid method for measuring them follows.

EXPERIMENTAL DETERMINATION

The dye suspension, containing the desired amount of caustic, is placed in the Dyeometer of the Dyeometer-spectrophotometer *(5)*, the platinum and saturated calomel electrodes are inserted, and the required temperature-control adjustment is made. A very thin transmission cell *(5)* is used so that commercial dye concentrations can be observed. When substances are required for stabilization purposes, they are introduced into the dyebath at the proper time. Hydro is then added in small portions until the dye is reduced, the potential is automatically recorded *(1)* and the spectrophotometric transmission curve is made. Potassium ferricyanide solution is then gradually added to oxidize the excess hydro while the potential is recorded continuously. At the same time the transmission of the solution at the wavelength corresponding to the absorption maximum is followed. When the first permanent change in the transmission of light due to oxidation of the dye is observed, the LP has been reached. In some instances hydro is consumed rapidly due to some unusual reactions in the dye solution and in those cases the additions of ferricyanide are not required. Figures 2 and 3 show curves of potential versus time. Curve A in Figure 2 is for a stabilized Blue BLD bath which needed no ferricyanide. Curve B in Figure 3 is for a Copper Brown bath which required ferricyanide additions. It may be observed that each such addition caused a lowering of potential. Should the first noted color change be a large one, then the determinations must be repeated using smaller portions of ferricyanide in the critical region. Sometimes the spectrophotometer need not be used and the LP can be taken as the potential at which the first precipitated dye particles can be visually observed to pass through the thin cell. It is preferable, however, to use the spectrophotometer to detect this small change.

The "leuco potentials" for a number of Calco dyes under specific conditions are tabulated in Table I. It must be emphasized that the "leuco potential" varies with dyebath conditions and that the values given are intended only as a guide. As can be seen from the data in Table I, the presence of nitrite influences the "leuco potential" value for some dyes but does not change that of others. This may well result from the effect of the nitrite on the rate at which equilibrium is established. It is suggested that the dyer correlate these values with those obtained under actual operating conditions.

PRACTICAL APPLICATIONS

As an example of the use of "leuco potentials", package dyeings have been successfully performed by maintaining the potential of the dyebath slightly above the LP. In these dyeings the initial reduction was accomplished with 0.5 oz/gal of caustic and very small quantities of hydro. During the dyeing the potential was held nearly constant by adding small portions of a dilute caustic and hydro solution. In this manner it has been possible to dye light shades at 200°F with a total hydro usage as small as 0.1 ounce per gallon.

In addition, dyeings have been prepared with minimum hydro consumption by utilizing the LP test papers described in Part II. This method of control requires careful attention and the choice of a paper which changes color when the potential of the bath is above the LP of the dye in use. The use of Vat Yellow G paper is often unsatisfactory since it will change color at potentials lower than the "leuco potentials" of most other vat dyes. Vat Golden Orange GD test paper has been found to be more satisfactory in most cases since its LP is appreciably higher.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Dr R H Kienle and Dr G L Royer for their help and suggestions. They also wish to thank their associates in the Application Research Department for their cooperation. Some of the potential measurements were made by Miss Carolyn Snyder.

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INDUSTRY—AMERICAN AND EUROPEAN PLAN*

RAYMOND W JACOBY

Ciba Co, Inc

IN AN EFFORT to aid industrial development in Europe, the United States Government, through ECA, undertook an extensive program wherein representatives of various industries in Europe were brought to the United States to observe practices followed here, and trained American men were sent to Europe to give assistance there. In contrast to this procedure were instances such as the one when the writer was invited by a large European textile organization to come over there to study and report on their operations from the American viewpoint.

Basically the study was one of comparisons and, as it progressed, the differences noted were so numerous that there was a tendency to become perplexed. When the study was completed, textile plants and other industries in several European countries were visited. In addition to this, discussions were had with people of various nationalities in all walks of life and considerable differences were constantly found to exist.

The differences in products, processes, and ideas become more amazing when one realizes the wide exchange of technical and trade publications, together with the extent of travel back and forth. A considerable period of time would be required to make a survey which would be broad enough to provide a basis for definite conclusions to be reached. On the other hand, certain opinions were formed which must be discussed in generalities, as specific details varied in each situation, but such generalities can indicate basic points. Where differences in ideas and practices exist between the two sides of the Atlantic, there is a tendency for each side to be critical of the other. Oddly enough, within certain limitations, both criticisms are justified. The reason for this is that most differences were not in basic principles, but more a matter of degree, with greater or less emphasis being placed on specific features. If a middle course was followed on each side, both sides would find themselves on extremely similar ground.

Raymond W Jacoby

How does European industry differ from American industry? This is the report of a study made by the author at the request of a European textile firm and the findings and results of this study.

It is not intended to convey the impression that these differences exist only between the two sides of the Atlantic. It is realized that similar differences exist in specific segments of industry in this country. These differences manifest themselves in the quarterly or annual statements of companies similarly engaged.

Further evidence of this fact is obtained if one reviews the history of any particular branch of production. Some companies have continued to operate successfully for decades, and during this same period many others have risen and passed into oblivion. In this discussion, differences between Europe and America are mentioned because they became apparent during a comparative study of operations.

It was very enlightening, as each individual factor was studied, to observe how it was dealt with and endeavor to ascertain the reasons which led to the situations being what they are. As there are many factors which affect business operations, and as conditions vary with each one, they will be discussed individually.

QUALITY

As to quality, no one disputes the skill of the European artisan. Furthermore, there are products and processes which require extreme skill, knowledge, and experience, as well as many hours of painstaking effort. For such items, the world always has and probably will continue to look to Europe. Their skill and knowledge have been supplemented by low wage rates which permit time to be spent on intricate details.

We would not like to admit that we, in this country, could not develop the skill required to manufacture such products. However, with our wage scales being what they are, our costs would be prohibitive if we expended the time necessary to produce such items. Of their quality they are justly proud, and we are glad to pay it tribute.

Their high regard for quality has become deeply ingrained, but one cannot help but feel that it has limitations. It can be carried to a point where it becomes impossible to compete in world markets in items where such extreme quality is not required. Undoubtedly, some of the principles embodied in the study of Precision of Measurements could be applied to this factor. One of these is that if variations of 1 or 2 per cent have no discernible effect upon the final product, there is no use controlling operations to the fourth or fifth decimal place.

Certainly no one should compromise with the desire for quality when the utmost in this regard is of advantage. Conversely, if the degree of quality sought after is in excess of that necessary, it is apparent that part of the effort is wasted. The American method of producing an item to meet the demands of end use has resulted in widespread industrial development.

It is obvious that no market can be sustained for any product which does not meet the requirements which it will be called upon to fulfill. On the other hand, it is realized that labor or material expended in excess of that necessary can result in such high costs that no market would exist for goods so produced.

Instances were encountered in Europe

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* Reprinted from *Dun's Review*, Sept, 1952.

Note: At the May 2, 1952 meeting of the Western New England Section (AATCC), Mr Jacoby presented an informal talk on his mission and exhibited numerous samples of fabrics and effects produced in Europe.

where more economical operations were resisted because it was felt that they could be carried out only at the expense of quality. It is admitted that there can be extremes in either viewpoint, but a middle course can be adopted which will be of benefit to all concerned.

While it is felt that some aspects of quality were over-emphasized, particularly in operating methods, other features of quality appeared to be overlooked. Satisfactory service to the consumer is an important item in quality. Undoubtedly, the American consumer of textile products has benefited materially by the introduction of the Sanforizing Process, whereby garments keep their fit after laundering.

This process has been widely adopted in the United States. It is interesting to compare the number of plants in the United States equipped to do this process with the number of plants similarly equipped in Europe. Recent figures show the number of such plants in the various countries to be as follows:

United States	107
Germany	14
Switzerland	9
France	8
Holland	6
Italy	4
Belgium	1

PRODUCTIVITY

The study and development of productivity is an important and vital feature of the activities of the former ECA, now MSA. Undoubtedly, this agency has and will continue to contribute valuable aid to Europe in this field. In some quarters in Europe the belief has been quite widely held that the only thing we think about in this country is production; everything else is sacrificed to attain this goal.

The constant thought of quality, referred to above, is one of the chief stumbling blocks in the path of increased productivity. The importance of productivity, or rather the result of the lack of productivity, was brought to mind very forcibly when a study of detailed costs was undertaken. A comparison of wage rates in the same operation showed that those in Europe were very far below those in the United States; whereas, the total costs per unit were higher.

Fuel costs are very much higher over there which, in turn, increases operating costs in industry. This subject is now receiving very serious study and, undoubtedly, constructive accomplishments will result. In the meantime, it appears logical to assume that part of the high cost of coal is due to low productivity.

In certain specific instances the differences in production per unit of time were quite astounding. In explanation of the low productivity many reasons were given. Some of them were valid, but they were not sufficient to provide the complete answer. After making allowances which were justified, there was still a wide gap. The only conclusions which could be reached were that the importance of this feature was not realized, and that intensive study had not been made to determine and eliminate every factor that reduced or interfered with maximum production.

In some of the instances studied, it was found that the speeds at which certain machines were operating were very much lower than here. Further investigations showed that the power drives installed were not of sufficient capacity to permit the machines to run at the speed at which similar machines operate in this country. This appeared to indicate that they considered our speeds to be unreasonably high.

In discussing productivity in one particular field, it was desired to make concrete comparisons on a particular type of equipment, so the production records of a similar American plant were examined. When this was done, it was interesting to see how the production per man-hour and machine-hour had increased in the United States during the past twenty years. It was an outstanding example, illustrating what has been accomplished in the United States when necessity arose.

An example of the difference in productivity is given in the American Productivity Team Report on The Belgian Cotton Weaving Industry which shows ratios of Belgium in the United States to be:

Population	5.5%
Cotton consumed	4.5%
Spindles	8.0%
Looms	11.0%

From this, it is seen that Belgium has 8 per cent as many spindles and 11 per cent as many looms to fabricate 4.5 per cent as much cotton as in the United States.

COSTS

It was quite a surprise to observe, as indicated above, that unit costs were higher even though wage rates were low compared to those in effect in the United States. In the instances observed, equipment was, in general, very good and well maintained. Technical processes and products showed the effect of well trained personnel.

It appeared, therefore, that high unit costs were due mostly to low productivity. Operating costs were broken down into three broad divisions: direct labor, direct material, and overhead. Direct labor costs were, of course, increased by the low production per man-hour.

Direct material costs were proportionate to production, so the local low productivity did not affect this item but, undoubtedly, low productivity on the part of suppliers increased the cost of materials to the plant consuming them.

Overhead includes some of the fuel and power, administration, management, taxes, insurance, interest, and depreciation. Most of these items are constant and are independent of production. They constitute a very large proportion of total cost and, with low productivity, the unit cost due to these charges becomes very high.

The sum of these three items resulted in high total unit costs, which explained the high prices of many articles. High prices together with low wages materially reduce the purchasing power of the individual consumer and, therefore, affect the entire economy.

One important factor in our industrial development has been our ability, through increased efficiency and incentive systems, to reduce costs and at the same time to increase individual earnings, thus creating a large consuming market. To attempt to achieve these two goals simultaneously appears to be inconsistent. Furthermore, a period of gradual inflation, with attendant rising prices, contradicts the idea of reduced costs. However, before the recent inflation started, there were many instances where this had been achieved. Also, during this period of inflation, there have been items whose costs have not increased as greatly as have those of the raw material and labor necessary for their production.

As an example, a standard textile fabric is a cotton print cloth which is 39 inches wide, has 80 warp threads and 80 filling threads per inch, and of which four yards weigh one pound. Such a fabric is described as 39"—80 x 80—4.00 yard print cloth. Comparative figures for this item in 1932 and 1952 are as follows:

Spot Price Raw Cotton	*Average Hourly Wage*	*Selling Price of Cloth*
June 1932— 5.20c/lb	$ .238c/hr	4.125c/yd
June 1952— 40.40c/lb	$1.190c/hr	19.750c/yd
Ratio 1952:1932— 7.77:1	4.98:1	4.79:1

From this, it is seen that while the price of cotton increased to 7.77 times and hourly wages to 4.98 times what they were in 1932, the price of the fabric increased to only 4.79 times the former price in the same period.

Apparently, through increased productivity and the adoption of an incentive system to increase earnings, similar progress could be made in Europe. Such progress is vitally necessary in order for them to expand their domestic market.

Accurate cost systems are necessary for the successful operation of any industry. The cost systems observed in Eur-

(Continued on Page 625)

Proceedings of the
American Association of Textile Chemists and Colorists

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September 29, 1952

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CALENDAR

COUNCIL

November 6 (Boston), Jan 16, 1953; April 17, 1953; June 5, 1953.

GENERAL RESEARCH COMMITTEE

(See Council dates)

NATIONAL CONVENTIONS

November 6-8, 1952 (Hotel Statler, Boston); September 17-19, 1953 (Hotel Conrad Hilton, Chicago); 1954 (Atlanta, Ga.); Sept 21-25, 1955 (Chalfonte-Haddon Hall, Atlantic City, N J).

MID-WEST SECTION

October 4, February 14 (Hotel Bismarck, Chicago, Ill); April 18 (Netherland Plaza, Cincinnati, O); June 20 (Outing, Lake Delavan, Wis); November 7, 1953 (Hotel Bismarck).

NEW YORK SECTION

October 24, November 21 (Kohler's Swiss Chalet, Rochelle Park, N J); January 30, February 27 (Hotel Statler, New York, N Y); April 17, May 22 (Swiss Chalet).

NORTHERN NEW ENGLAND SECTION

December 6 (Annual Meeting, Lowell Textile Institute).

PACIFIC SOUTHWEST SECTION

October 4 (Outing, Ojai, California).

PHILADELPHIA SECTION

Oct 24 (Penn Sheraton Hotel); Dec 5, Jan 16 (Kugler's Restaurant).

RHODE ISLAND SECTION

Oct 24 (Providence Engineering Society); December 5 (Annual Meeting, Sheraton-Biltmore, Providence, R I).

SOUTH CENTRAL SECTION

December 6 (Patten Hotel).

WESTERN NEW ENGLAND SECTION

Oct 3, Nov 14 and Dec 12 (Rapp's Restaurant, Shelton, Conn).

OTHER EVENTS

AMERICAN SOCIETY FOR TESTING MATERIALS

1953 Annual Meeting, June 29-July 3, Chalfonte-Haddon Hall, Atlantic City, N J.

AMERICAN STANDARDS ASSOCIATION

34th Annual Meeting, November 19, Waldorf-Astoria, New York, N Y.

ISO—TC 38 (Textiles)—SC-1 (Color Fastness), Nov 10-11 (ASA Headquarters, New York, N Y).

AMERICAN TEXTILE MACHINERY ASSOCIATION

Exhibit of American Textile Machinery, April 26-May 1, 1954, Atlantic City Exhibition Hall, Atlantic City, N J.

INTERNATIONAL COTTON AND RAYON EXHIBITION

Sept 27-Oct 12, Busto Arsizio, Italy.

INTER-SOCIETY COLOR COUNCIL

Nov 5 (Pepco Auditorium, Washington, D C).

NATIONAL ASSOCIATION OF HOSIERY MANUFACTURERS

41st Knitting Arts Exhibition, April 27-May 1, 1953, Atlantic City Auditorium, Atlantic City, N J.

NEW YORK BOARD OF TRADE (DCAT)

27th Annual Drug, Chemical and Allied Trades Dinner, March 5 (1953), Waldorf-Astoria, New York, N Y.

TEXTILE RESEARCH INSTITUTE

23rd Annual Meeting, Nov. 17-18, Hotel Commodore, New York, N. Y.

Philadelphia Section to Meet with P-W Color Group

THE Philadelphia Section, in conjunction with the Philadelphia-Wilmington Color Group, will hold its next meeting at the Penn Sheraton Hotel, 39th and Chestnut Sts, Philadelphia, Pa, on October 24th.

Speaker for the meeting will be Dr Deane B Judd, chief of the Colorimetry Unit of the National Bureau for Standards, on the subject "Color Formation, Color Measurement and Color Blindness". Dr Judd has been a member of the Photometry and Colorimetry Section of the NBS for more than 20 years.

Constantin J Monego, Chairman of the Philadelphia-Wilmington Color Group, will preside at the meeting.

As an added attraction, several autographed copies of Dr Judd's recently published book "Color in Business, Science and Industry" will be awarded.

ASA Subcommittee to Meet Nov 10-11

SC-1, a subcommittee of TC 38 (Textiles) of the International Standards Organization, will meet at the headquarters of the American Standards Association on November 10th and 11th. SC-1 is devoted to the subject of color fastness.

CORRECTION

SEPTEMBER issues of the *Reporter* have carried an erroneous date in the Calendar for a future meeting of the Mid-West Section. The last named meeting of the current schedule should correctly read November 7, 1953 (Hotel Bismarck). *There will be no meeting of the Section on November 7th of this year.*

The next regular meeting is set for October 4th.

R M Evans to Address ISCC in November

AT A jointly-sponsored meeting of the Inter-Society Color Council on Wednesday, Nov 5 in the Pepco Auditorium, 10th & E, NW, Washington, D C, Ralph M Evans, secretary of the ISCC and an outstanding authority in the field of color will present a talk entitled "The Expressiveness of Color." At present the meeting is under the sponsorship of the Washington-Baltimore Colorists and the Washington Chapter of the Washington-Baltimore Colorists.

Further information on the meeting may be obtained from Waldron Faulkner (1200 18th St, NW, Washington 6, D C), a member of the Executive Committee of the ISCC and current Chairman of the Washington-Baltimore Colorists.

An abstract of Mr Evans' talk follows:

"Using color photography to investigate the problem and to illustrate the points, an attempt is made to find the basic factors in the use of color in all situations. The various kinds of color are first reviewed. This is followed by a study of why color is used and the various ways in which it may affect people. Emotional, associative and expressive elements are considered, leading to the conclusion that deliberate expression is the most important case. The rules of color harmony are reconsidered from this standpoint.

Harmony is one feeling that can be expressed by color but the rules, basically, refer to the form of the expression rather than the thought. The expressive elements of color are shown not to be simply hue, saturation, and lightness but to include all attributes and all modes of appearance of color. In these terms it is possible to generalize the concept of color schemes and at least make a start toward a true understanding of the ways in which the power of color may be applied successfully."

Special Communication———

APPLICATION OF ULTRASONICS TO TEXTILE PROCESSES*

ARTUR ALVES de ARAUJO
Textiles Rudyart, S de R L
Mexico City, Mexico

INTRODUCTION

ULTRASONIC energy has found important applications in industry in the past few years, and more recently many applications in all branches of science and technology have been achieved.

This paper is merely an attempt to review the matter dealing with the phenomena of high-frequency sound waves with special emphasis on the ultrasonic effects more directly concerned with their application to textile processes and to give to those interested in doing research in this field a guide to the subject. In doing so I have given the chief place to experimental results, and have taken account of theoretical work only when this has been necessary to a proper understanding of the subject.

The application of ultrasonics to textile processes is an open field for research because of the very relations between ultrasonic effects and the phenomena that are involved in many of these processes, such as emulsification, reaction acceleration, dispersion, crystalline structure, diffusion and many others.

With the recent development in ultrasonic equipment, a variety of new laboratory equipment is available to open the way to widespread experimentation and to new industrial applications of ultrasonic energy.

ULTRASONIC EFFECTS

The term *ultrasonics* is used in acoustics to denote frequencies that are beyond the limits of the human ear (*1*).

The laws valid for the audible range, that is to say, frequencies up to 20 khz (kilohertz, or thousands of cycles per second), also hold for the ultrasonic range, but in the latter case further phenomena take place which are not observed in the audible range.

Because of the shortness of ultrasonic sound waves (the shortest ultrasonic vibrations are of the order of magnitude of visible light), it has been found possible to make use of ultrasonics in many directions.

A A de Araujo

This paper is a presentation of the great possibilities of successful research in the field of high-frequency sound waves for application to textile processes. For this purpose, the matter published in the last years on ultrasonics has been reviewed, and particular attention has been given to those effects that are likely to be of direct application to the textile industry.

It is emphasized that the science of ultrasonics offers a number of possibilities for the solution of a great number of problems in textile processing and for the improvement of techniques in textile dyeing and finishing.

By using modern methods of generation it is possible to produce vibrations up to a frequency of about 5×10^5 khz (*1*).

DISPERSIVE AND COLLOIDAL—— It was shown as early as 1927 (*2*) that intense ultrasonic waves transform immiscible liquids, such as water and oil or water and mercury, into very stable emulsions. By use of very great ultrasonic power very fine emulsions of various metals were recently produced and also of various oils and paraffins in water; some metals were obtained with particles so small that true colloidal solutions were obtained.

An optimum time of exposure was observed by Mozovskii and Poloskii (*3*) for each given energy above which further exposure caused coagulation of the sol.

PHYSICAL AND CHEMICAL——Szalay (*4*) succeeded in splitting up a number of highly polymerized molecules by ultrasonics of a frequency of 722 khz. The action of ultrasonics on gels was investigated and it was found that thioxotropic gels were liquefied in exactly the same way as by shaking. No permanent change was produced in the gel. The swelling and peptization of gels in liquids of any sort is also accelerated by the action of ultrasonics (*5, 6, 7*).

Ultrasonic energy increases the speed of some reactions. The oxidation of dyes was observed by Beuthe (*8*). Hydrogen peroxide was produced after ten minutes' action of ultrasonics on pure distilled water (*1*). Prudhomme and Grabar (*9*) explained the formation of hydrogen peroxide by electrical discharge in the interior of the cavitation voids causing a photochemical decomposition of water and the formation of hydrogen peroxide.

DEGASSING AND OTHERS —— The formation of gas bubbles when ultrasonic waves of relative energy are sent through liquids was observed for the first time by Boyle and Lehman (*10, 11*). These bubbles are driven towards the nodes of a stationary sound wave, and, according to them, are produced by the union of microscopically small bubbles already present in the liquid.

Danser and Newmann (*12*) explain the agglomeration of aerosols by ultrasonic energy by theorizing that sound waves cause the small particles to vibrate, thereby increasing their normal collision rate. The particles on collision will adhere to each other. By a series of collisions and subsequent adhesions small particles can be agglomerated. Campbell and Long (*13*) studied this effect on emulsions. Ultrasonic vibrations can increase the relative movement of dispersed particles and hence can increase their rate and energy of collision with each other and consequently their rate of coalescence, thus decreasing the stability of the emulsion.

Moses (*14, 15*) describes how organic coatings are separated from both metal and nonmetal substrates by longitudinal ultrasonic vibrations. Also pointed out are the great promises of this method which may be readily applicable to many types of materials other than those used in this

* A special communication to the *Proceedings* from the author while he was a student at the New Bedford Textile Institute.

investigation (metal to metal, metal to wood, metal to plastic, and plastic to glass).

EFFECTS ON FIBROUS CELLULOSIC MATERIALS——Morehead (*16*) studied the effect of ultrasonic waves on the disintegration of cellulose fibers before and after hydrolysis. The effect of ultrasonic vibrations on both native and regenerated cellulose fibers is to break them down into thin, almost electron optically transparent fibrils, the length and width of which depend on the type of fibers. Particles instead of fibrils result if the fibers are subjected to acid hydrolysis, followed by ultrasonic vibration. The size and shape of the two types depend upon whether they originate from native or regenerated fibers. Particle dimensions are shown in the electron microscope to be in good agreement with the viscosity data and are apparently related to the crystalline and amorphous structure of the original fiber.

The influence of ultrasonic waves on the transformation of hydrated cellulose to natural cellulose was investigated in Japan by Kubo (*17*). The transition from hydrated to natural cellulose is made much easier by the preliminary application of ultrasonic waves to the material immersed in a polar medium. The effect is due to the destabilization of the crystal lattice by mechanical vibrations. When the transition treatment is carried out on a molecular compound of hydrated cellulose after applying ultrasonic waves, the interference point of natural cellulose in X-ray pictures begins to show itself at lower temperature then in the sample without such preliminary treatment.

These phenomena are based on the action of ultrasonic waves in stimulating the solvation and in increasing the mobility of hydrated cellulose molecules. The temperature of transition is greatly influenced by the change in the degree of solvation.

In Sweden, Aktiebolag (*18*) treated lignocellulosic material to aid the separation of cellulose. Lignin-to-cellulose bonds are broken by subjecting wood and other lignocelluloses to supersonic vibrations (300 kilocycles per sec). Exposing wood powder to such vibrations for 1 minute permits 55% of wood to dissolve in Schweitzer's reagent. Longer exposures up to 10 minutes have no additional effect. The ultracentrifuge shows that 50% of the material going into solution is cellulose.

Gralen and Berg (*19*) also concluded from their experiments that the treatment of wood with ultrasonic waves causes a disintegration of the biostructure of the wood and a splitting of the bonds between the lignin and cellulose molecule. After treatment with ultrasonics, about 50% of the wood can be dissolved in cuprammonium. The dissolved material (carbohydrates) consists of two main components with different sedimentation constants. The components are thought to correspond to the cellulose and hemicellulose of the wood.

Simpson and Mason (*20*) observed that treatment of small batches of wood pulp with ultrasonic waves had effects similar to those of beating, except that no cutting occurred. No loss in viscosity was found. The power consumption, although not directly measurable, was many times that of a beater used to produce the same effect. Ham (*21*) also studied the effect of ultrasonic waves on fibrous cellulosic materials, submitting an aqueous suspension of finely divided fibrous cellulosic material to the action of ultrasonic vibrations of a frequency of about 50 to 9,000 khz.

APPLICATION TO TEXTILE PROCESSES

One of the most interesting applications of ultrasonic energy is upon the increase of the rate of dyeing.

Before an attempt is made to describe how the rate of dyeing could be increased by ultrasonic vibrations, a very brief description of the phenomena that takes place in dyeing will be presented.

When fiber is placed in an aqueous dyebath, phenomena preceeding the dyeing operation appear, the swelling of the fiber being the most outstanding of all (*22*). Water molecules penetrate into the intermolecular spaces of the amorphous matter of the fiber. This swelling effect is more pronounced at higher temperatures because of the increase in the molecular vibrations and the spreading apart of the molecules tied up by covalence forces. This same phenomenon appears simultaneously with the diffusion of the molecules and ions dissolved in the dye bath into the swollen fiber.

There are really three stages in a dyeing operation (*23*): First, diffusion of dye in aqueous dyebath to fiber surface; second, adsorption of dye on the micellar surfaces of the outer surface of fiber; and, third, diffusion of dyestuff towards the center of fiber.

The last step above is by far the slowest and the most important, being responsible for penetration, fastness to washing and crocking, etc.

Diffusion of dye inside a fiber is much slower than in external solution because of the greater mechanical obstruction to movement presented by the crystalline portion of a fiber structure and also because of the restraining forces between fiber and dye. Because of unequal adsorption of ions, micellar surfaces of fiber must acquire an electrical charge with respect to solution, and in consequence similarly charged ions are repelled from the surface and oppositely charged ions are attracted to it. These forces are opposed by thermal agitation of the solution, which tends to produce a uniform distribution of all ions (*23*).

It seems likely that the rate of dyeing could be greatly increased with the aid of ultrasonic vibrations by reducing the restraining forces between dye and fiber, by increasing the rate of movement of dye inside the fiber, by greater impact of dye molecules on fiber surface, and by increasing the diffusion rate. Rath and Merk (*29*) have found that rate of dyeing is increased more for cellulosic fibers than animal fibers. The dyeing of hydrophobic fibers is also promoted by sound waves.

These restraining forces could be reduced by the electrolytic dispersion described by Claus (*24*), this electrolytic method causing a motion tending to produce a uniform distribution of all the electrolytes in the solution. The rate of movement inside the fiber will probably be increased by the effect of ultrasonic vibrations on the activation of dye molecules and on the structure of the fiber; greater impact may be secured by the activation effect, and the diffusion rate is likely to be increased by the above-mentioned effects and the loosening action of ultrasonics on the crystalline structure as shown by Hollman and Bauch (*25*).

The diffusion of a solute through solids or liquids differs from diffusion through gases in being generally much slower and having a much higher temperature coefficient. The average velocity of the molecule is of the same order whether it is in a gas, liquid or solid, but in the latter two cases it spends most of its time vibrating to and fro, only occasionally breaking free and moving on. The theory of activated diffusion explains the high temperature coefficient of diffusion through solids by supposing that solute molecules remain vibrating about an equilibrium position until they chance to acquire, by random exchange with neighboring molecules, a certain critical energy. They are then in an activated state and are able to overcome the restraint of their surroundings and move or diffuse (*23*).

This activated state can be brought about by ultrasonic energy, which furnish the vibrating molecules with the critical energy they need to break their static equilibrium and thus to diffuse.

At the same time these molecules are excited by this ultrasonic vibration and, furthermore, are driven by the sound waves from this equilibrium position (*1*). This same radiation pressure of ultrasonics will increase considerably the impact of the molecules on the surface of the fibers that, together with the electrolytic dispersion,

will aid the adsorption on the micellar surfaces.

The loosening in the crystalline structure is of great significance in speeding the rate of diffusion. This loosening of structure was used by Mahoux (*26*) to improve and speed up nitrogen hardening of steels.

The rate of diffusion of nitrogen into steel is very small at temperatures commonly used. The depth of penetration is considerably increased, according to Mahoux, under the action of high-frequency sound waves, and penetration also takes place more quickly.

This loosening effect in the crystalline structure is of very great significance in increasing the rate of diffusion. Therefore dyeing operations could be carried out more efficiently and at lower temperatures with the use of ultrasonics.

This effect on the structure is probably the explanation of the effect of ultrasonic energy on the chemical bonds and in the intermolecular bonds such as the Van Der Waals type.

Breaking these bonding forces, and in so doing loosening the crystallite structure, the dye molecules will have greater movement inside the fiber, that means better and more even penetration of the dye molecules in the fiber.

The diffusion of dye in the aqueous dyebath to the fiber surface and the uniformity of the dyed mass of material are helped by the dispersive effects of ultrasonic energy as described in the preceeding pages. This same effect is likely also to have an influence in the rate of diffusion inside the fiber towards the center because of the small size of the particles during ultrasonic dispersion, as shown below.

Russia and Japan have been carrying out research in this field and results described below are some published in the last few years.

Dispersion of Indanthrene dyes by means of ultrasonic waves has been studied by Morozov and Milinskaya (*27*). Indanthrene Green GG (0.15 —0.30 g in 50 ml of water) was exposed to the action of ultrasonic waves for 15-60 minutes. The quality of suspension obtained was evaluated by dyeing samples of mercerized satin with it and measuring the intensity of the colors in the Strelkov colorimeter. The size of the dye particles reached 1-2 microns during dispersion. A preliminary grinding of the dye does not facilitate its dispersion. Replacing water with a solution of NaOH, hydrosulfite, etc, has no effect on the degree of dispersion but produces a poorer dyeing.

In order to determine whether alternate compression and relaxation can aid the dyeing of cotton, the effect of an ultrasonic field was studied by Sokolov and Tumanskii (*28*). It was found that in all cases penetration was greatly improved, the yield per bath and bath utilization were improved, and the speed of dyeing was considerably increased. In insoluble azo-dyes the ultrasonic field can be used directly upon the soluble azo to eliminate poor dyeing properties.

In the very recent studies carried on by Rath and Merk (*29*) on the influence of sound waves on dyeing very interesting results were obtained showing definite advantages accruing through the use of sound waves as compared with normal techniques. It was shown that the use of sound waves increased greatly the rate of dyeing and decreased considerably the dyeing temperature needed for the attainment of the same deep shades as obtained at higher temperature without the presence of sound waves. Better leveling and penetration were also obtained.

Polotskii (*3*) studied the effect of gases on the dispersion of dyes in the ultrasonic field and noticed that the treatment of dyes in the field of ultrasonic waves in the presence of air at a pressure above 100 mm of Hg promoted and stabilized the formation of highly dispersed suspensions (dyes-water).

Another effect with interesting application to textile processes is the orientation of growing crystals under supersonic waves. Orientation experiments which show the evolution of distinct nodal planes in a supersonic field were described by Kapuskin (*30*) and application to rayon processing has been patented by Calhoun (*31*).

Calhoun used high-frequency waves to control the uniformity and degree of re-orientation of the crystallites of regenerated cellulose fibers (viscose, cellulose esters). Sound waves of a frequency of 1,000 to a million or more cycles per second accelerate the diffusion of the acid-setting liquid and the dexanthating liquid through the fibers and control the uniformity of such diffusion in all portions of the fiber. The control of dexanthation by choice of the frequency and magnitude of the waves, the duration of exposure of the fibers to the vibrations, and the stage in the manufacture at which the waves are applied, allows the fibers to be stretched while the cellulose is only partially but uniformly dexanthated, a condition giving optimum orientation of the crystallites.

Sound waves, generated by any suitable means, may be applied either directly or indirectly to fibers, threads or yarns at all stages in manufacture, from the time of their formation to just prior to subjecting them to the usual after-treating processes, or at any one or more of such stages. At this same time a method and a machine were patented by Peterson and Dart (*32*) for controlling the uniformity of crystallite formation in regenerating cellulose by means of high-frequency waves.

A wool-like rayon fiber ("Delamare-Zellwolle") was produced by the application of vibrational energy (*33*). In 1950 photographs of Delamare type viscose staple-fiber and of wool were published in which some resemblance to the scale surface of the latter can be seen in the former. The scale-like surface was produced by means of various types of vibratory apparatus. Gernet (*34*) claims that wool-like rayon may be produced by an ultrasonic field with periodic condensing and rarifying action imposed on the pump-generated pressure before the spinning nozzle.

American Viscose Corp (*35*) patented a method for production of alkali-cellulose of uniform composition by subjecting pulp in contact with alkali solution to high-frequency sound vibrations, and in 1951 Tomberg (*36*) described the effects of ultrasonic irradiation on the coagulation of cellulosic solutions and on the quality of the cellulosic lump obtained after regeneration. Also, a method of slowing down the coagulation and regeneration rate is described.

Calhoun (*37*), taking advantage of the aglomeration effect of ultrasonics, made another interesting application of high-frequency waves to the rayon process. A method and its application were patented for continuously clarifying the acid-setting bath for viscose by high-frequency sound waves. Sound waves of frequencies similar to those used above are propagated, by suitable means, in the contaminated bath after it has been drawn from the extrusion zone and an intermediate tank into a regenerating or reconditioning system in which the relative proportioning of the constituents of the bath are readjusted to condition the bath for re-use. A sound-wave irradiation zone may be established in the path of the bath liquid beyond the point of extrusion of the viscose. This procedure aggregates the usually microscopic particles into larger or microscopic particles, which settle rapidly; a clear solution results in a second or minute as compared with hours required for normal setting. The sediment may be removed continuously by any suitable means, and the liquor may be filtered by conventional methods. The spinning bath may be degasified prior to the propagation of the sound waves to prevent dissipation of vibrational energy by bubbles of gas, such as H_2S, which may occur in the bath.

Taking advantage of the same effect, Wiczer (*38*) designed a device for washing soiled textiles in which the goods are subjected, for 1 to 20 minutes, to the action of a scouring liquid (preferably continuously changed) which is excited by

ultrasonic waves at a frequency of 16,000 to 30,000 cycles per second.

The disintegration of cellulose (*16*) by ultrasonic energy was used in electron-microscopic investigations of cellulose fibers by Wuhrmann, Heuberger, and Muhlethaler (*39*). Present methods of preparation of cellulose fibers for electron-microscopic investigations tend to modify the original structure. Consequently, interpretation is very difficult and results disagree with those obtained by other methods.

It was found by Wuhrmann and co-workers that exposure of cellulose fibers, such as ramie, hemp, cotton, to intense supersonic fields for 3 to 10 min yield extraordinarily fine fibrils without structural modification. Fibers barely observable microscopically are further resolved under the electron microscope to within 60-70 A. A microphotograph of ramie, hemp, and flax after 10-minute supersonic treatment and an electron-microscopic photograph (X 14,000) of ramie and hemp were shown. There is no uniform fiber size, and dimensions are solely a function of the intensity of the treatment. No preferential cleavage flows are apparent.

Mathieu-Sicaud and Levasseur (*40*) studied the dispersion of clay suspensions by ultrasonics and interpreted the results with an electron microscope. The effects of the frequency of ultrasonic waves on the dispersion of kaolinite and montmorillonite suspensions in water were studied by nephelometer and electron microscope. It was found that the dispersion varies with the frequency, reaching a maximum at 960 khz for kaolinite and at 320 khz for montmorillonite. The mean particle size was 1000 A in the former case and 1700 A in the latter. Each frequency corresponds to a certain mean particle size. Ultrasonic dispersion is superior to that produced by chemical means, e g, stabilization with NH_3 for producing kaolinite sols.

This dispersive effect is likely to have a large application in finishing and printing in making homogeneous pastes and suspensions. In the paint industry (*41*) ultrasonic energy was used to obtain satisfactory pigment dispersions of North Standard fineness 8, and studies were made on pigment concentration, viscosity, amplitude of vibration, and time of treatment.

Other applications of ultrasonics are the production of spinable fibers from plant stalks (*42*). Stalks containing fibers are roasted, steeped in a liquid and acted upon by ultrasonics.

The Societe Anonyme des Manufactures des Glaces et Produits Chimiques de Saint-Gobain (*43*) applies ultrasonics in the production of glass fibers. Glass fibers in viscous or plastic states are subjected to the action of sonic or ultrasonic vibrations.

Rath (*44*) describes some applications of the gentle agitation of sound waves in textile finishing. Sound waves are used in rapid cleaning (in which case felting is reduced), dyeing, and removing mechanically adhering dyes.

CONCLUSION

If we recollect the various effects of ultrasonics so far discussed and compare them with the phenomena that take place in some textile processes, it is easy to see the great potentiality of ultrasonic energy as an aid to speed those processes and to improve ther techniques.

In dyeing, ultrasonics have great possibilities in increasing rate of dyeing, improving penetration, yield per bath and bath utilization, in elimination of poor dyeing and in allowing dyeing at lower temperatures.

In the manufacture of artificial fibers, ultrasonic energy has application in controlling the uniformity and degree of reorientation of the crystallites of regenerated cellulose and artificial fibers, in the production of wool-like rayon fibers, in the acceleration of the coagulation of viscose-rayon filaments as they come from the spineret, in continuous clarifying of the acid setting bath for viscose, and degassing viscose solutions. It is likely to have successful use in laundering and cleaning textiles as in laundering soiled fabrics, removing graphite from nylon, and cleaning raw cotton and wool.

Highly dispersed pigment pastes, clay suspensions and finishes could be prepared by ultrasonic waves to aid the printing and finishing processes. High-frequency waves will also be a great aid in electron-microscope investigations and in testing the dynamic properties of filaments, yarns and cords.

It is also easy to believe that ultrasonic energy will play an important role in reducing the tendency of wool to felt and shrink as well in the extraction of fibers from plant stalks, and other textile processes, such as bleaching, scouring, desizing.

At the present time there are some difficulties from the standpoint of equipment, techniques and information in carrying on successful research in the study of possible future uses of high-frequency waves. In spite of the recent development in ultrasonic equipment and the publication of technical literature, a lack of ultrasonic apparatus suitable for industrial use does not permit, for the time being, a transition from laboratory to industrial scale.

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Herbert F Parkinson—Dyer & Chemist, Renfrew Woolen Mills, Renfrew, Ont. Sponsors: E V Burnthall, F Schlaeppi.

Haldee L Reed—Dye Chemist, American Enka Corp, Enka, N C. Sponsors: R M Stribling, J B Foster, Jr.

Carl A Setterstrom—Sales Mgr, Textile Fibers, Carbide & Carbon Chem Co, Division of Union Carbide & Carbon Corp, New York, N Y. Sponsors: P J Wood, A L Snyder.

Robert K Sponagel—Mfg Chemist, Vat Dyestuff Plant, Ciba States, Ltd, Toms River, N J. Sponsors: L P Bauer, G Wiseman.

George Susich—Scientist, Research and Development, Philadelphia Quartermaster Depot, Philadelphia, Pa. Sponsors: C J Monego, J F Oesterling.

Newton A Teizeira—Research Associate, Fabric Research Labs Inc, Boston, Mass. Sponsors: E R Kaswell, G Thompson.

Geoffrey R Ward — Research Chemist, General Aniline & Film Corp, Easton, Pa. Sponsors: C F Jelinek, G M Gantz.

William B Whitley—Asst Overseer of Finishing, Erwin Mills, Cooleemee, N C. Sponsors: E P Lavoie, T E Hastings.

Samuel Wood — Overseer of Finishing, Cons Textile Co, Windsor Div, North Adams, Mass. Sponsors: M Fishman, H A Lamoureux.

JUNIOR

Odell A Adams—Dyer, Copeland-Fowler Fin Plant, Burlington, N C. Sponsors: J P Franklin, W C Privette.

Howard J Helms, Jr—Sales Representative, Westvaco Chem Div, Food Machinery and Chemical Corp, Charlotte, N C. Sponsors: J W Ivey, P C Thomas.

Robert M Holthouser, Jr — Sales Rep, Nova Chemical Corp, New York, N Y. Sponsor: R S Funke.

Harold B Sturtevant, Jr—Trainee, Joseph Bancroft & Sons Co, Wilmington, Del. Sponsors: G W Bell, W M Hemphill.

ASSOCIATE

Gardner R Alden — Research Division Mgr, Dennison Mfg Co, Framingham, Mass.

Frank V Connolly — Representative, United Waste Co, Inc, East Dedham, Mass.

Joseph Weber — Textile Technologist, Mandee Fabrics Inc, New York City, N Y.

SENIOR

LeRoy C Thompson—Gen Mgr & Vice Pres, Hussong-Walker-Davis Co, Philadelphia, Pa. Sponsors: J P Conaway, B C Bond.

Applications for transfer to Senior Membership:

Dorothy M Achey — Richard E Milana
Charles M Barrett — Charles J Wolhar
Warren E Lincoln, Jr

Millson, Sisson to Speak at October Meeting of Mid-West Section

THE October 4th meeting of the Mid-West Section, to be held at the Bismarck Hotel, Chicago, Ill, will feature outstanding speakers at both sessions. The afternoon session will also see the election of Sectional officers for the forthcoming year.

Helen Sisson, formerly fashion coordinator for Marshall Field & Co and currently fashion director for Phoenix Hosiery Company, will speak on "The Interdependence of the Dyer and the Stylist" at 2 pm.

In the evening Henry Millson, assistant director of the Application Research Department, Calco Chemical Division, will discuss "Microscopical Dyeing Phenomena, Studies with the Microdyeoscope".

EMPLOYMENT REGISTER

This column is open for two insertions per year, per member, without charge. Blanks can be obtained from, and filed with, the Secretary of the Association, Lowell Textile Institute, Lowell, Mass. It is understood that these will be open to inspection by prospective employers who can obtain further information from the Secretary.

52-20

Education: Lowell Textile Institute, BTC.

Experience: Textile chemist and colorist, wool, nylon and wool blends.

Age: 38; married; references.

9-29, 10-13

NOTICE TO AUTHORS OF PAPERS

MANUSCRIPTS for the *Proceedings* and for other publications of the American Association of Textile Chemists and Colorists shall conform to the requirements and standards given in this *Notice,* which was drawn up after considerable study. Before publication, manuscripts for the *Proceedings* shall be approved by the Editor, not only for editorial correctness according to the standards of this *Notice,* but also for content of technical matter. In his work, the Editor may enlist the aid of anonymous reviewers who are selected for expert knowledge in particular fields.

It is presumed that authors in studying the comments of reviewers and of the Editor will remember that all recommendations are made in a kindly, helpful, sympathetic manner to improve the paper in both literary and technical excellence. Although authors should cheerfully consider suggestions, they are expected to defend their position if justified, especially when strictly technical matters are involved with which the authors have an intimate knowledge.

MANUSCRIPTS—Manuscripts shall be typewritten double-spaced with approximately one-inch margins on 8.5 x 11-inch white paper. In addition to the original, at least one carbon copy is required. Pages are to be numbered consecutively with Arabic numerals, and each page after the first shall carry the authorship at the very top. Tables and figures shall also be numbered consecutively, the tables with headings containing Roman numerals as TABLE I, TABLE II, etc, and the figures with Arabic numerals as Figure 1, Figure 2, etc, appearing *below* the figures. The names of the authors and their laboratories or business connections should appear below the title of the paper.

ARTICLES APPEARING IN THE "PROCEEDINGS" IN RECENT ISSUES OF THE "AMERICAN DYESTUFF REPORTER" will be helpful to authors as models of form for the typing of manuscripts.

LITERARY STYLE AND FORM OF PRESENTATION—In the writing of papers, authors are requested to observe a trenchant, simple style of writing directed to textile chemists and colorists with at least an elementary knowledge of chemistry, physics, mathematics, engineering, textile processes and textile machinery.

In the organization of the material, there should be one or more introductory paragraphs setting forth the occasion, significance and main objectives of the paper and of the method of attack. This should be followed by the body of the presentation, either with discussions interspersed throughout this portion or with a collected section marked "DISCUSSION" after the main body of the paper. Finally, there shall be a brief section at the end entitled "SUMMARY" or "CONCLUSIONS."

Center headings should be employed sparingly and generally will include only very important section headings, such as "INTRODUCTION," "EXPERIMENTAL," "DISCUSSION," "CONCLUSIONS," "SUMMARY," and "REFERENCES." Side headings (see third paragraph of this *Notice* for an example) shall be indented and run into the text to which they apply, and shall be separated from the paragraph by a dash. The publisher will print center headings in bold-face capitals and side headings in capitals.

LITERATURE REFERENCES AND FOOTNOTES—References to the literature and all footnotes (except those in tables) shall be numbered consecutively with underlined Arabic numerals in parentheses at the proper place in the text. Where a reference or footnote is to be used again, the original number is simply repeated; this obviates the necessity of repeating the footnote or reference at the bottom of the page. References to the literature shall conform to the universal usages followed by *Chemical Abstracts,* which include underlining of book and journal names to indicate italicization in printing.

The spelling and rules of punctuation followed in manuscripts shall be those found in the *Merriam-Webster New International Dictionary;* abbreviations and chemical formulas shall conform to *Chemical Abstracts.* Periods shall be used only at the end of sentences, not after abbreviations.

FIGURES AND GRAPHS—Figures and graphs should be black line drawings on white drawing paper. Photographic prints are acceptable, preferably glossy prints on double-weight paper. Duplicates should be available for dispatch to reviewers. Diagrams and graphs should preferably be designed in long form to cover one column of print but may be two columns wide or the width of a full page where necessary. In graphs the frame and actual curves should be inked more heavily than the co-ordinate lines, and these latter should not be too close together. Various styles of broken lines are sometimes desirable to distinguish curves. Experimental points should be given with small plane figures, such as circles, squares, diamonds or triangles. Numbers and legends on co-ordinate axes are to be lettered in the graph by the author. Numbers and titles of figures should be placed below the diagram or on the edge of the back. Each piece of illustration copy should bear on the margin or on the edge of the back the name of the author and the title of the paper.

Photographs of authors should be included with copy, to be run in conjunction with the paper. These must be on glossy stock, and should be large enough for proper reproduction.

TABLES—Tables should not be used indiscriminately because they are very expensive to set up in type. They should be designed to be one column, two columns or three columns wide. Tables should be arranged with the view of conserving space; column headings should be short and abbreviated. Quantity designations shall never appear in the body of the table but in the headings. Tables, if possible, should be placed in the manuscript where they belong rather than separately.

SYNOPSIS—A separately written synopsis of not over 200 words containing the gist of the subject matter must accompany every manuscript.

GALLEY PROOFS—Galley proofs will be sent to the author by the publisher for correction before publication. This should not be interpreted as an invitation to rewrite the paper but rather as an opportunity to correct errors.

REPRINTS—Fifty reprints of papers published in the *Proceedings* will be furnished without charge by the publisher if requested when galley proofs are returned. These reprints are printed on one side of the sheet only and then stapled together. A schedule of prices of reprints in the usual form accompanies the galley proofs.

OWNERSHIP OF COPYRIGHTS AND PATENTS—All papers presented at general meetings of the Association or at meetings of any of its local sections and all communications shall become the property of the Association. Such papers are not to be published elsewhere until they have appeared in the *Proceedings* of the Association. Papers published in the *Proceedings* are copyright by the Association. Any patentable disclosures shall of course remain the property of the author or authors.

TRADE-MARKS — As the AATCC wishes to co-operate in the protection of trade-marks, a list of all trade-mark names mentioned in an article will be placed in a separate paragraph ahead of the list of references. The author will therefore prepare such a list in capital letters under a center heading entitled "TRADE-MARKS", under which should appear the following sentence: "The following names used in the article above are trade-marks for the kinds of products for which the generic name follows the trade-mark name:"

To simplify editing and printing, it is requested that, in the body of the article, trade-mark names be written with only an initial capital letter and with no other references.

Courtesy demands that authors include competitive products as well as those of his firm. Many current trade-mark names are to be found in the *AATCC Technical Manual and Yearbook.* Examples of how trade-marks should be given in the paragraph for trade-marks are as follows:

ORLON, an acrylic fiber
NIAGARA, a direct dye
IGEPON, a synthetic detergent.

Rhode Island Section——

THE COMMISSION-DYEHOUSE LABORATORY*

ARTHUR W GROVER
Enterprise Dye Works, Inc
Woonsocket, R I

The laboratory of a well-managed commission dyehouse that dyes and finishes textiles in various stages of manufacture containing many different fibers has a great responsibility in developing and controlling the many procedures necessary in handling such a variety of work, besides the responsibility of testing the chemicals, dyes, fibers, supplies and water used in such an enterprise. The chief chemist gives some details concerning the duties of the laboratory and cites interesting examples of special problems that have occurred during his experiences.

INTRODUCTION

THE PLANT——In order that you may realize the variety of work in a commission-dyehouse laboratory, I should like to explain the various departments of our plant.

First, there is the top-dyeing department. Here are handled all types of fibers in top form, such as wool, rayon, mohair, nylon, Dacron polyester fiber, Vicara zein fiber and Dynel. Chrome, metachrome, soluble-vat, metalized, sulfur, union, and direct dyes are the usual classes of dyestuffs used to dye the various fibers. This department also does vigoreaux printing on top. Vigoreaux printing is used mostly for light shades because the final blend is much more even in color than when dyed and undyed top are blended together. Another operation is treating top by the Cluett-Peabody Sanforlan chlorination process under the S W Patent. It is also equipped to do bleaching, mothproofing, and fireproofing.

The second department is devoted to dyeing and finishing cotton jersey for the rubber-shoe trade. Here direct and developed dyes are used.

The third department handles piece goods. It dyes and finishes all kinds of fibers separately or blended in fabric form. Our machinery is equipped to dye and finish woven cloth, tubular knit jersey, and upholstery cloth. We have a range where we apply various resin finishes and carry out pigment dyeing. In this department the same kinds of dyes and developers are used as in the top department.

We have about 200 active accounts to take care of, each of whom is always in haste to get deliveries. As soon as any goods or samples are received, the customer wants to know his delivery date. Many times customers will send in a half-inch-square sample for a shade to be matched and a six-inch square of cloth on which to make a sample dyeing and expect to see the results by return mail.

When a new shade is received, it is checked in the dyehouse files for a similar shade on the same type of fabric. If there is any question, the fabric and shade are sent to the laboratory to be matched. Since the first of the year we have matched 600 separate shades. Two-thirds of these for the dyehouse and the other one-third for customer approval before dyeing.

With such a diversification of fabrics and fibers, one can realize the great importance of the laboratory.

LABORATORY

The laboratory does various routine testing as follows:

1) Spot-testing and checking dyestuffs and chemicals. This is to evaluate our purchases against standards and similar product samples. An interesting test in example of this was matching a brown shade on a rayon and acetate fabric leaving the acetate clear. In the course of testing two similar direct red dyestuffs, we found one left the acetate clear while the other stained.

2) Moisture control on top is important for two reasons: First, we must put in as much moisture in the top as was received because top is bought on regain basis and, secondly, the moisture is needed to get better spin and yield.

3) Tests on Sanforlan. Treatment for effectiveness of felting on top or fabric.

4) Tests on percentage of fibers in fabric and top. Here we have found that the procedure as outlined by Harold W Wolf *(1)* very accurate in determining the percentages of the new fibers.

5) Testing of bleach baths for batches of either top or fabric in the dyehouse. This is important because of the danger of damage to wool if too much peroxide or alkali is used. We have found the use of phosphates in bleaching baths very valuable in sequestering iron and other metallic salts. The combination of peroxide and fluorescent dyes gives desirable results when required.

6) We spot-test fabrics and top for oil to compare the amounts in the unfinished and finished products as a check on the efficiency of our scouring compounds.

7) Light, washing, rubbing, perspiration, and other fastness tests are run as required. We test only when necessary, usually when new fibers and fabrics are being developed.

8) Matching shades for the dyehouse. In the selection of dyestuffs, cost is paramount.

MATCHING SHADES —— In all cases of shade matching, we prefer to work on a fabric after it has had the preliminary treatment that the pieces themselves are to obtain before dyeing. If it is a wool fabric and the finish calls for fulling and scouring, the ¼ yard that the laboratory works with is previously wet-finished in a similar manner.

In the case of blends where the prefinish is a desize and a boilout in a kettle, we work on a heading similarly processed. This gives a truer shade and makes the laboratory fabric similar to the dyehouse pieces. It also helps penetration in many fabrics.

If an entirely new fabric is presented to us, a fiber-identification test is made with one of the several identification stains available from dyestuff companies. A good stain reveals how various fibers are woven in a fabric and if unexpected fibers are present. Many times we find acetate instead of rayon, or cotton specks in worsted fabrics, which require covering with a speck dye. Recently we had a fabric which was supposed to be all-nylon. When a fiber-identification test disclosed the presence of silk specks, we had to use different dyes than usual to cover the silk fibers.

Two other quick tests for fiber identification are Alizarine Blue SAP (CI 1054) and Direct Black. The latter is used mostly to detect acetate.

In all our dyeings we use American Woolen multifiber test cloths both in the

* Presented before the Rhode Island Section at the Providence Engineering Society in Providence, R I, on May 23, 1952.

laboratory and dye house. This gives us a guide as to how the various fibers are dyeing.

Certain techniques have been found to be helpful according to the dyestuff used. In dyeing navies with top-chrome colors, distilled water is used. When we used river water or city water, it was difficult to get repeat dyeings of the same shade. Most of the time the colors would be flat and wouldn't chrome to their true brightness, or they would go violet in tone. In a dye kettle a solution increases in volume from the condensation of steam to heat the bath; in a dye pot the bath decreases from evaporation and water has to be added frequently. This gives a concentration of metallic ions in the bath which affect dyestuffs sensitive to metals.

After an investigation we found, when using city water, that the tone of a chromed dyeing became more violet from the presence of copper in the water. The copper came from a continuous hot-water system we have in the laboratory. Chlorine in the city water reacted with copper tubing to give copper chloride, which gave the purple cast. The flat cast came from iron in the river water.

To dye a shade of navy on some fabrics, ammonium acetate with distilled water was used. This was to help penetration and give more level dyeings. It was found that, with some colors such as Chrome Blue Black RSS, the zinc-free type of Blue-Black and Chrome Black T, the true shades of the color were not attained. When we ran comparative dyeings, starting with acetic acid and distilled water, the true shades obtained indicated that the ammonium acetate not only retarded the color but gave a flat shade.

In top dyeing with Chrome Blue-Blacks and Blacks it is common practice for many dyers to exhaust with formic or sulfuric acid. Many of the dyestuff companies recommend this procedure, as formic or sulfuric acid clears the bath. We ran tests on dyeings dyed with acetic acid only versus dyeings dyed with acetic and then exhausted with formic or sulfuric acid. There was very little color difference. The difference showed when the top was given a fulling test; the multifiber test cloth for the acetic-acid-dyed sample was clean and white, while the sample exhausted with formic or sulfuric acid stained the multifiber test cloth yellow. This proved to us that, though the bath cleared on the addition of formic or sulfuric acid, the dyestuff deposited itself on the outside of the fiber and washed off during the fulling operation. Our fulling test, by the way, is very simple. A pad is made of the top to be tested and attached to it is a piece of multifiber test cloth. The sample is submerged overnight in a porcelain casserole containing 6 ounces of soap and 3 ounces of soda ash per gallon. In the morning it is washed and examined for staining.

In dyeing metalized colors on a fabric in a dye kettle, dyeings usually came up on the red side, lacking yellow as compared with laboratory dyeings. This we found to be due, first, to the yellow component, which was usually the last to dye, and, second, to the temperature in the dye kettle of about 190° compared with a boiling temperature for laboratory dyeings. We have recently had several of our kettles enclosed. This gives a higher temperature, and the results are closer to laboratory dyeings.

UNION DYEING———Union dyeing is certainly the most interesting and yet the most difficult of all types. We try to select colors that work well together and give the desired results. Penetration, which is rather difficult to obtain on some fabrics in union dyeing, is improved by raising and lowering the temperature. Many of our union dyeings require a CRF or melamine finish, requiring selected dyestuffs which will stand these various finishes.

We try to give true shades to the dyehouse whenever we can, by running duplicate dyeings and dyeings without adds. We find that adds on a laboratory sample are not always accurate.

REDYEING ——— Redyeing constitutes an important part of our work and right after the last war we stripped and redyed over a million yards of government cloth back into civilian shades. This included 18-oz suitings, 16-oz shirting, kerseys, elastiques, and a 32-oz overcoating material.

In our redye work we set up certain procedures to follow. First, we run tensile tests for strength before redyeing. Second, we ascertain if any finishes are present, such as CRF, waterproofing, etc. Third, we run fiber-identification stain tests.

If the new shade can be made on the old without stripping, we give a 5% ammonia treatment at 160° before redyeing. This helps to even up the fabric. It neutralizes the fabric if it is in an acid condition.

When a fabric has to be stripped in order to make the shade, we usually proceed as follows: First, a 20% ammonia treatment at the boil. This stripping is usually effective for most unions and acid dyes. Then the pH is watched carefully as it is lowered the color starts to dye back on the cloth.

If ammonia is not effective for stripping, we use sodium sulfoxite with acetic acid followed by a neutralized bath of ammonia at the boil.

As wool dyed with metalized dyes become very tender when stripped with sodium sulfoxite, a titanium stripper is then used. This does a fairly satisfactory job in most cases.

Other types of stripping agents we have used are peroxide, hydrosulfite, soda ash, chrome and oxalic acid, sodium sulfate, and sodium bisulfite. Stripping with sulfoxite makes wool more receptive to many direct dyestuffs and complicates the selection and application of dyes in redying unions.

OTHER LABORATORY DUTIES ———All finishes and dyeing procedures are developed in the laboratory before plant trials. The laboratory then has direct supervision of all resin finishes run on the range. It develops and controls all pigment-dyeing processes. It controls the plant's water system, which consists of a soda-ash-alum-flock apparatus with pressure filters and a zeolite system. The laboratory also controls boiler feed water under the direction of one of the companies supplying boiler-feed-water treatments.

Further to illustrate the duties of our laboratory, I give you the following instances:

A) One of the most complicated jobs we ever did for the Top Department was right after the war when nylon was scarce. One of our customers bought some garnetted parachute sliver in top form. In order to match the standard of the nylon then being produced it was necessary to scour, bleach, tint and deluster the nylon. This was added to the cost of the customer's nylon, which at the beginning cost 25c more than the regular nylon-top staple.

B) A mill mixed lots of Sanforlan-treated top and untreated top. We tried various ways to distinguish the two and finally came up with a fiber-identification stain that showed the difference.

C) We were asked to speck-dye nylon garnetted filament yarn in a wool/nylon stock-dyed cloth without affecting the ground shade. Here we found the Capracyl dyes did a good job.

D) We helped develop the Army-Blue shades, one of which later became the Air Force 84 shade.

E) We matched a shade called Emmence on a worsted challis for Cardinal Spellman to wear to the College of Cardinals at Rome. This had to be fast to light and perspiration.

REFERENCE

1) Wolf, H W, *Am Dyestuff Reptr* 30, No 9, 273 (1951).

HOTEL RESERVATIONS FOR CONVENTION CLOSE OCTOBER 20

HARRY M HARTNETT, Chairman of the Convention Hotel Committee, has announced that all hotel reservations must be made by October 20th for the forthcoming National Convention in Boston.

Regular hotel reservations for members and guests will be handled solely through the AATCC Housing Bureau, Boston Chamber of Commerce, 80 Federal Street, Boston 10, Mass.

The Committee has been assured that adequate hotel accommodations will be available for everybody; however, members desiring suites or reception rooms should communicate directly with the hotel. THESE ARE NOT HANDLED BY THE COMMITTEE.

A schedule of prices for rooms which have been reserved is at the bottom of this page.

Members are asked to indicate their choice, with full information on a reservation card which has been sent out by the Committee. It is requested that the reservation card be returned at once along with the accompanying registration envelope (a reproduction of which appears on this page).

You will receive an acknowledgment from the Bureau and a confirmation from the hotel than can supply your accommodations. If acknowledgment is not received by October 24, notify the Bureau at once.

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MEMBERS—JUNIORS	3.00		
MEMBERS—LADIES	6.00		
MEMBERS—STUDENTS	FREE		
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OLNEY AWARD LUNCHEON—NOV. 7	5.00		
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MAKE CHECKS PAYABLE TO A.A.T.C.C. CONVENTION

I PLAN TO HAVE _____ LADY GUESTS AT THE CONVENTION.

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	Single Room	Twin Bedded Room	Double Bedded Room
HOTEL STATLER	$5.50 to $10.00	$10.50 to $16.50	$9.50 to $13.00
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HOTEL TOURAINE	$5.50 to $6.50	$8.75 to $12.00	$8.25 to $10.50
SHERATON PLAZA	$5.85 to $9.85	$11.00 to $15.00	$8.80 to $15.00
HOTEL BRADFORD	$5.75 to $6.75	$9.95 to $13.00	$8.50 to $9.50

ALL ABOVE RATES ARE PER DAY PER ROOM

Reservations will not be held after 6 P.M. any day

Industry——

(Continued from Page 612)

ope did not go into as much detail as is customary here. While it is realized that sometimes cost systems are too elaborate, they can also be too simple to provide much necessary information. The existing situation may be due, in part, to the function which the cost system is to perform.

There, the principal consideration seemed to be to provide total costs as a basis for establishing prices. In this respect, it is very useful; but an equal, if not more important feature of any cost system is the providing of information so that efficiency can be improved. If overall cost figures are high, details of such costs are necessary in order to determine where economies can be effected. This valuable feature of a cost system did not appear to receive sufficient consideration.

SELLING

In the United States, selling is a technique just as vital to successful operation as any other factor. In Europe, it seemed to be more incidental. They may feel that it is sometimes overdone here, but undoubtedly the skill, ability, energy, and ingenuity exerted in this field in this country is a major factor in our industrial development. Here, again, a difference in viewpoint is very apparent.

In Europe, the basis for consideration is the actual market, whereas, here, our efforts are expended not only in that field, but also in the potential market. One argument against increased productivity was the lack of a market, and instances were encountered where surprise was created when it was suggested that as much skill and effort be exerted in selling as there was in production.

Much of their discussion centered on the population of the various countries, with the explanation that the large population of the United States provided an enormous market. To illustrate that much more than the number of people was involved, it was cited that, on the basis of population alone, India or China should far exceed the United States in industrial development.

HUMAN ENGINEERING

When the average European reads of the industrial strife in this country, he is prone to think that our human relations are poor. He overlooks the fact that, in the cases of industrial conflict which are of such magnitude as to make the front pages of the newspapers, only an insignificantly small percentage of our workers are involved. Personal observation has never, through the years, revealed an industrial executive who did not have complete respect for the dignity of man, and who did not consider that his position was one more of responsibility than of authority.

The idea of team-work permeates our various activities, and no individual can engage in team-work unless he really is a member of the team. Our conception is that no sub-division, whether it is a major branch of a large organization or a small department, is a unit unto itself. Each unit serves only as an integral part of the whole. Each unit affects, or is affected by other units and, therefore, must function as a part of the over-all picture.

To accomplish this, we emphasize the individual's importance as a component part, and through group activities, enable him to co-ordinate his efforts and responsibilities with others who are involved. In this country, frequent meetings are held wherein aims, efforts, and possibilities are discussed and teamwork carried out. It was very surprising, therefore, in the situations encountered, to find such procedures lacking in Europe.

It has been said that every company is the lengthened shadow of one individual. This shadow can be lengthened only when it extends downward through the organization's structure to each individual employee. Contacts and consultations provide not only the means of accomplishment, but encourage effort and co-operation as they enable all individuals to realize their importance. If a person feels that he is just an individual, and not a vital, component part of an organization, his morale suffers as do his efforts.

In Europe, a few situations arose where it was possible to encourage efforts by indicating the importance of the individual, and the response was so instantaneous, complete, and enthusiastic, it gave conviction that much more could probably be accomplished in this field.

SIGHT-SEEING

No matter how pressing the demands of business activities are, one finds time to see much that is of interest. One receives a new conception of antiquity when he sees a building bearing markings indicating it was built in 1621 and, while commenting on its age, has his attention drawn to a structure across the square which was built in the twelfth century. There is much of sheer beauty, much to make one realize the architectural and engineering skill that existed centuries ago. There are many evidences of undertakings which were stupendous in their day. They all arouse tremendous admiration.

One day the library of Louvain was visited. One could spend hours looking at both the exterior and interior. As we walked away our hostess said, "Just think, twice in my lifetime this beautiful thing has been destroyed." Then a terrible thought came to mind—all the people whom we had met, and with whom we had talked, had known either directly or indirectly, suffering, privation, hardship, or tragedy. Many of these things which we had been admiring—the canals of Amsterdam and Burges; the Castle of the Counts in Ghent, started in 600 AD containing a torture chamber and instruments of torture; other castles situated at strategic points and surrounded by moats; walled towns; massive stone gates guarding the approach to settlements—were not built to be admired centuries later. They were built for protection.

They were monuments of man's inhumanity to man. Then came the realization that this had been their heritage, not just for centuries, but for over a thousand years. It made one pause and think. It made one wonder what our attitude would be if we had such a heritage, and had about us always such constant reminders of man's cruelty through the ages.

AID TO EUROPE

Early 1952 was not an appropriate time to consider aid to Europe from an unbiased viewpoint. Having just paid the adjustment on 1951 Income Tax and started on 1952 payments, made one realize how much our Government's activities were costing. Considerable of the funds were going to Europe but, nevertheless, it was desirable to consider the expenditures objectively. Just as progress was being made at various times, we would pass some reconstruction work and hear a companion say, "Part of this is your money." However, we still tried to find the answer.

So much had been read and heard on both sides of the subject we often wondered whether, even while there seeing the people and the countries, we could make a proper appraisal. Yet, we wanted to do so.

KEY TO HAPPINESS

With this thought in mind, we were constantly looking for anything which might be significant. One of our last evenings in Europe was spent with a couple who had few of the comforts and none of the luxuries which we take for granted, and whose lives, by our standards, would appear to be dreary and commonplace. One could not help but wonder what life held for them, yet they appeared to be happy. Finally, we asked, "What do you do for pleasure?"

With a voice filled with enthusiasm, the husband answered, "Every weekend we get outdoors. We put the children in

a school where they will be taken care of. We ski."

Then we asked what they did in Summer when they could not ski, to which he replied that they climbed mountains. We understood that skiing is exhilarating, but wondered about mountain climbing, so we said, "Is that fun?"

"Oh, yes," he answered, "It is wonderful. We work for several hours. It is hard work. We have to be very careful of every step. Finally, we get to the top and then we sit, and look, and think and talk." Then a wonderful light came into his eyes as he continued, "You know, that is as near to God as one ever gets in life. As we sit there, my wife and I say to each other, 'If only the politicians could come up here; come up here like we did—the hard way; work and struggle like we did; and then sit down and look and think; we would have a better world in which to live'."

Then we knew we had found the answer. We realized that if, with such a heritage, a spark of faith and hope like this still endures, then any aid which we can give to keep it glowing is necessary if civilization, as we know it, is to survive.

• PATENT DIGEST •

PAUL WENGRAF

EMBOSSING CELLULOSIC RESIN IMPREGNATED TEXTILES G, 4

U S Pat 2,593,207
(Betex Sales Corp——Silver——April 15, 1952)

The inventor states that raised embossed effects can be obtained by the following procedure:

1) Impregnate with a solution of a polymerizable resin, preferably of the N-alkoxymethylpolyamide type. Soluble in aqueous alcohols, e g, 60% isopropanol plus 40% water, this type is exemplified by Du Pont Type 8 DV 55 or 45 Nylon Resins (see U S Pat 2,443,450 in references below).

2) Partially dry the impregnated goods to a moisture content of (preferably) 15% at temperatures not exceeding 250°F.

3) Emboss the partially dried fabrics at a temperature of 275-350°F. The steel embossing roll carries the raised design; the other (platen) roll is made of paper. These are operated before use to form "mating" indentations.

4) Treat the embossed fabrics in a chamber that is heated to the curing temperature required for the resin applied.

Example: 1) Impregnation is carried on with a 2% solution of Type 8 DV 55 Nylon Resin in 70% isopropanol—30% water, mixed with 2% citric acid (calculated from the resin's weight).

2) The fabrics are squeezed to a pick up of 85% and dried at 180°F, still leaving 15% moisture in the goods.

3) Through a pair of "female and male" embossing rolls (as described above) at 275°F the fabrics are pressed at a speed of 15 yards per min.

4) Curing is carried on for 8 min at 275°F.

Other curable resins, such as methylated methylolmelamines (e g, Aerotex), or urea-formaldehyde condensates may be used under modified conditions. A wash-fast, resin-impregnated embossed fabric of improved tensile strength results, according to a table inserted in this specification.

Among other references cited by the Patent Office:

U S Pat 2,526,637 (Du Pont/1950): shrinkproofing wool by preparing first with a polyamine (synthesis from ethylene oxide, carbon monoxide and ammonia), and thereafter with formaldehyde (cf *Am Dyestuff Reptr 40,* 198 (1951)).

U S Pat 2,504,857 (Bancroft/1950): crease-resistant cotton fabrics obtained by impregnating with mixtures of methylolmelamine and methylated methylolmelamine (cf *Am Dyestuff Reptr 39,* 524, (1950)).

U S Pat 2,443,450 (Du Pont/1948): coating flexible articles, such as leather or textiles, with N-alkoxymethyl polyamides, obtained by reacting linear superpolyamides with an alcohol and formaldehyde.

U S Pat 2,430,866 (Du Pont/1947): producing granulated N-substituted alkoxymethyl polyamides for use as thermosetting compounds.

U S Pat 2,121,005 (Raduner—Bener): embossing calender effects by impregnating with a urea-formaldehyde condensate, drying at moderate temperatures, embossing and curing; thus, a similar process, using carbamide-resin solutions.

DYEING WOOL with Chromatable Dyes—— Diammonium Phosphate and Ammonium Sulfate Added C, 4, 06

U S Pat 2,593,850
(Victor Chem Works——Coleman, Coté——April 22, 1952)

The one-bath chrome dyeing method is generally carried out in a dyebath containing a chromate (e g, neutral sodium chromate), Glauber's salt and ammonium sulfate, in addition to the dyestuff. The bath is first adjusted to a slightly alkaline condition to swell the fibers and promote penetration. Gradually acid is added during heating to form the dye-chromium lake within the fiber. A very close control of the pH values of the bath during this operation is necessary in order to achieve uniform results. A final pH of 5.2-5.8 is desirable to develop and fix the mordant color.

Difficulties have been experienced in this standard method because the bath must be cooled before addition of the acid, and also because the acid is added locally in this process and thereby distributed unevenly, causing poor levelness.

A gradual and automatic decrease of the pH value throughout the dyebath, coming from inside the bath without outside addition, is necessary to improve the uniformity of the dyeing, according to the specification. It has been found that reliable results can be expected by using a potentially acid agent diammoniumphosphate, combined with ammonium sulfate. The initial pH value of the dyebath containing diammoniumphosphate—about 7.5 (optionally adjusted with ammonia to 7.8)—drops during heating to 6.2-6.5. Certain dyestuffs are fully developed under these conditions, but for others an endpoint of pH 5.2-5.8 is optimal. In this event, an addition of acid is necessary. The introduction of free acid has to be avoided; thus, in the final stage the necessary acid conditions result by addition at the start of ammonium sulfate, which has little buffering effect in itself.

Tables show the regular automatic decrease during prolonged dyeing at elevated temperatures. Chrome Fast Blue BX for instance, a dye which otherwise requires very careful control of pH-conditions, can be dyed satisfactorily with 1% of dye, 30% of ammonium sulfate, 5% of diammonium phosphate and 1% of sodium dichromate; the pH drops from 7.5 to 5.4 within 165 minutes.

Ready-made compositions for use in

this one-bath chrome-dyeing process consists of ammonium sulfate (55.6-93.8%), diammonium phosphate (3-36%) and the mordant salt (2.5-15.8%).

Among other references cited by the Patent Office:

Am Dyestuff Reptr of Aug 23, 1948 (Panel meeting, Northern New England Section, pages 547-8) discusses the advantages of diammonium phosphate in acid and/or chrome dyeing due to the increase of the pH value of a 5% solution from 7.85 to 5.78 during the boiling process.

J Soc Dyers Colourists of Dec, 1945 (E I Noble, pages 328-33) deals generally with pH control in dyeing processes and particularly with the advantage of using phosphoric acid and ammonium phosphate in acid- and chrome dyeing.

POLYAZODYES——Aliphatic Amines and Copper Complex Compounds Added C, 4, 01

U S Pat 2,594,803
(Ciba Ltd——Riat, et al——April 29, 1952)

This patent refers to the dyeing of cellulosic fibers with water-soluble polyazodyes, which form metal (copper) complex compounds of difficult solubility. Dyestuffs that are particularly suitable to the present method contain, in addition to two or more azo groups, one or more other azo groupings that link hydroxylated or carboxylated nuclei, preferably in symmetrical arrangement. Formulas for a great number of appropriate dyes are presented in the specification.

The copper-free dye is first dissolved in the dyebath, after which ammonia (or preferably an aliphatic amine or alkanolamine that cannot be volatilized by steam) and a copper salt containing copper in the anion in complex form, e g, copper sodium tartrate or copper glycollate, are added. The amine should be added in an amount at least sufficient to form the complex salt if the latter is to be formed in situ in the dyebath from a water soluble copper salt, e g, copper sulfate.

The present invention is said to give superior results as compared with a one-bath after-coppering method, as described in Ciba's U S Pat 2,148,659 (see references), by considerably shortening the dyeing process and providing better control during the dyeing operation.

Example: a dyebath is prepared from an orange tetrazodye and some sodium carbonate. A solution obtained from copper sulfate, sodium citrate and monoethanolamine is added after which a wetted cotton fabric is entered and the bath temperature raised to the boil within one half hour. After boiling for another ¾ hours, during which time some Glauber's salt is gradually added, the dyebath is exhausted. It is suggested that a solution of a condensate of dicyanodiamide and formaldehyde be added to the last rinsing bath.

References cited by the Patent Office:

U S Pat 2,185,905 (Ciba/1940): Di- and polyazodyes derived from diazotized aromatic amines and phenols, which give sparingly-soluble metal complexes, are applied on vegetable fibers first under strongly alkaline conditions after which alkaline metal salt (copper salt) solutions are added. An alternative method consists of dyeing with metal complex azodyes for at least part of the dyeing process under alkaline conditions.

U S Pat 2,148,659 (Ciba/1940): dyeing azodyes at the boil, then adding the complex-forming metal solution, e g, alkaline Cr- or Cu salt solutions, to the same bath to form the sparingly-soluble azodye-metal compound within the fiber.

Further reference is made to U S Pat 2,526,106 (cf *Am Dyestuff Reptr 40,* 198 (1951)), which covers a dyeing method in the presence of copper complex salts and dicyanodiamide formaldehyde condensates.

Some of the dyestuff brands described in the present specification are mentioned in Ciba's Brit P 670,522 (April 23, 1952). They also have to be used in the form of their metal (Cu-) complex salts for dyeing cellulosic fibers. Despite evident analogies in the dye constitutions, as reported in both patents, the essential difference is that the method covered by the British patent provides for a different dyeing procedure: the ready-made (sparingly-soluble) copper complex compounds of the direct dyes are covered with hot water and then refluxed at the boil with ammonia or a lower amine. Surprisingly th base enters the complex, forming submicroscopic dispersions—even true solutions—in water. The solubilized complexes are dyed from soda ash-Glauber's salt solutions giving light- and washfast dyeings. It is indicated that the amine-containing complexes are not very stable; they apparently decompose in the dyeing process whereby the metalliferous dye is fixed in the fiber as an insoluble pigment, while the base breaks away.

PRINTING VAT DYES Thickened with Water-in-Oil Emulsions D, 2, 01

U S Pat 2,594,899
(American Cyanamid——Fordemwalt——April 29, 1952)

The preamble to this invention discusses disadvantages arising from customary vat-printing methods that use starch-gum thickeners. These were found to alter unfavorably the hand of the printed material and must therefore be removed before finishing. Moreover, it is said that the color yields are not always satisfactory. With this latest patent, the inventor aims at eliminating thickeners of this type.

A solution to this problem has been found in replacing the standard thickening agents with emulsions of the water-in-oil type. It is surprising to find that these emulsions are stable despite the content of electrolytes necessary for developing the vats. The inner-aqueous-phase may contain dispersing agents, e g, lignin sulfonate, without any of the usual aqueous thickening agents. The emulsion may contain 10-50% (preferably 15-20%) of the oily phase comprising a low viscosity liquid hydrocarbon of about 80-400°C (preferably 135-175°C) distillation range in which a drying oil modified thermosetting alkyd resin is dissolved. It is suggested that a solution of the aforementioned dispersing agent be emulsified in a solution of the resin dissolved in part of the hydrocarbon, and that this emulsion be homogenized with the remainder of the hydrocarbon solvent. Finally the aqueous solution of alkaline and reducing agents has to be stirred into the oily phase and homogenized therewith. Further procedure, i e, drying after printing, steaming, reoxidizing, soaping and rinsing, is analogous to standard vat printing processes.

Example: sodium lignin sulfonate is made into a concentrated aqueous solution that is stirred into a 50% solution of an alkyd resin (prepared from 33% of phthalic anhydride and 55% of linseed oil) in a hydrocarbon solvent in the distillation range of 135-175°C. The main part of the hydrocarbon solvent is added and after thorough homogenization an aqueous solution of potassium- or sodium carbonate, sodium formaldehyde sulfoxylate and glycerine as well as a commercial color paste of vat dye C I 1184 (e g, Ciba Blue 2 B) are stirred in and further homogenized until a smooth paste results. The prints made with this paste and fixed as usual appeared to be brighter and stronger than those prepared with the same amount of fixing ingredients and a commercial starch thickener.

References cited by the Patent Office:

U S Pat 2,288,992 (Interchem Corp/1942): textile printing with water-in-oil emulsions containing solvent-soluble cellulose ethers in a volatile hydrophobic solvent (e g, hydrocarbons) as the continuous phase and an aqueous solution of a water soluble dye (e g, Rapidogen Red) in the dispersed phase.

U S Pat 2,288,261 (Interchem Corp/1942): incorporating a phosphatide such as soybean lecithin into the oily phase of an emulsion printing paste to prevent the migrating of leuco vat dyes from the aqueous into the lacquer phase. The

aqueous phase contains Rongalite, glycerin, glyecin and potash.

U S Pat 2,202,283 (Interchem Corp/1940): pigment-printing emulsions consisting of a water-immiscible film-forming liquid, e g, a solvent soluble alkyd resin, in the outer phase and an aqueous dyestuff solution in the dispersed phase.

Reference is further made to U S Pat 2,267,620 (Interchem Corp), which refers to an emulsion printing paste: the inner (aqueous) phase contains a dye-discharging composition e g, Ponsol Blue GD, glyecin, glycerine, potash and Rongalite; the outer phase contains a fiber-forming solute, e g, ethylcellulose, in organic solvents, such as xylene plus Solvesso. This differs from the present patent in that the paste is primarily intended to provide colored discharges and that the oily phase contains solvent-soluble alkylcellulose instead of the modified alkyd resins, which obviously have a superior effect.

ABSTRACTS

Man's Synthetic Future

Roger Adams, *Science* **115**, 157-63, February 15, 1952.

(Excerpts from that portion of the article which deals with textiles)

Cotton, silk, and wool have been the fibers used almost exclusively for fabrics until a few decades ago. Rayon and acetate silk were then introduced. These are both chemical modifications of cellulose, derived usually from cotton or wood. In spite of the fact that they lack many of the desirable properties of the natural fibers, particularly wet strength and recoverability of the original shape upon drying, these fibers have been widely accepted and have supplemented or in part replaced cotton and silk.

About fifteen years ago nylon, a strictly synthetic fiber, made by combining very simple molecules into a complex one similar to those nature furnishes us, made its appearance. Chiefly because of its rapid-drying properties, its durability, and its resistance to fungi and insects, it has found many applications for which natural fibers are not suitable. Natural silk, for which nylon is a substitute, has never recovered its pre-war status.

Newer synthetic fibers have appeared on the market—e g, Orlon, Acrilan, Dynel, which resemble one another somewhat in properties and are all based on the same simple chemical, acrylonitrile. These fabrics are utilized particularly for seat covers, curtains, and filter cloths in industry. They are also suitable in the apparel field because of their smart appearance, long wear, and easy laundering. Still another synthetic fiber is Dacron, which resists wrinkling, water, and moths as does no other fiber. Suits made of Dacron go through rainstorms without losing their crease, and can be cleaned with soap and water without losing their original shape after drying.

Rapid drying is effected because the threads or fabric do not absorb water, and drying consists merely in the evaporation of surface moisture. But this nonabsorption of moisture leads to a certain amount of discomfort, particularly in hot weather. To find a fiber that will dry rapidly and at the same time permit moisture to penetrate is asking more than the chemist is likely to discover, since they are two incompatible properties. But these synthetic fibers must be improved in other ways, or new fibers found which have the desired properties, before natural fibers will be extensively replaced.

The author predicts the discovery of synthetic fibers which the public will prefer for most purposes to the natural fibers. An official of the wool industry made a statement recently that the demand for wool as a fabric will never be replaced. These words were spoken by one completely unfamiliar with the potentialities of chemical research. Just as the automobile replaced the wagon, synthetic fibers will replace the natural fibers. Half the wool now consumed will be replaced by synthetic fibers within ten to twenty years, the time being dependent primarily on the restrictions which industry encounters in materials and money for plant construction. Synthetic fibers to replace cotton will also be discovered; these will be strong, durable, and moisture-absorbing, thus making them suitable and comfortable for wearing apparel. They will not, however, be rapid drying.—WHC

The Search for New Polymers: Dye Affinity and Tensile Strength

J A Somers, *British Rayon & Silk J* 29, 51-2, July, 1952.

Persistent efforts during the past half-century to produce stronger artificial fibers have been rewarded by conspicuous success, and it is now possible to make fibers having about twice the strength of real silk. But with this success has come a measure of disappointment, for the stronger fibers are made, the more difficult it is for the dyer to color them. The problem of today is to discover a means for making artificial fibers so that they have both a high tensile strength and a good affinity for dyes.

Stronger fibers are made by stretching them during or shortly after spinning. As the stretching is carried to a greater degree, so is the affinity of the fibers for dyes reduced correspondingly. Viscose rayon which has been only moderately stretched has one advantage over ordinary viscose—in blends with cotton it no longer dyes heavier than the cotton.

The author states that in making the fibers now commercially available, nylon is usually stretched 300 per cent, Vinyon N 1200 per cent, Terylene 400 per cent, and Orlon 600 per cent.

The difficulty of dyeing stretched fibers is not so much that the fiber absorbs dyes less rapidly as that the amount of intramolecular space capable of receiving dye particles has been contracted. With a highly stretched fiber these changes may make it impossible to dye really deep shades.

Stretching of fibers is used to bring the long chain molecules parallel to each other and to the length axis of the fiber, and also to bring these long chain molecules close together laterally. Both of these changes contribute to the increased tensile strength.

The author points out that long chain molecules must not be considered as being perfectly straight. Most of them are knobbly and twisted. The closeness with which they can be packed in the fiber by stretching is governed to a large extent by this irregular form. To preserve a sufficient amount of space within the fiber for the dye particles to penetrate it is suggested that the fiber should be made from a synthetic polymer having molecules more than usually irregular, or with atomic groupings attached at spaced intervals such that in the stretching the lateral packing of the parallel aligned molecules is hindered.

Another method of improving the dyeing properties of these stretched fibers is to ensure that there are present a large number of atomic groups (OH, NH_2, COOH, CO-NH, etc) which have an affinity for dyes.

The author believes that progress in the manufacture of strong fibers with good dyeing properties will be made by development along these lines.—WHC